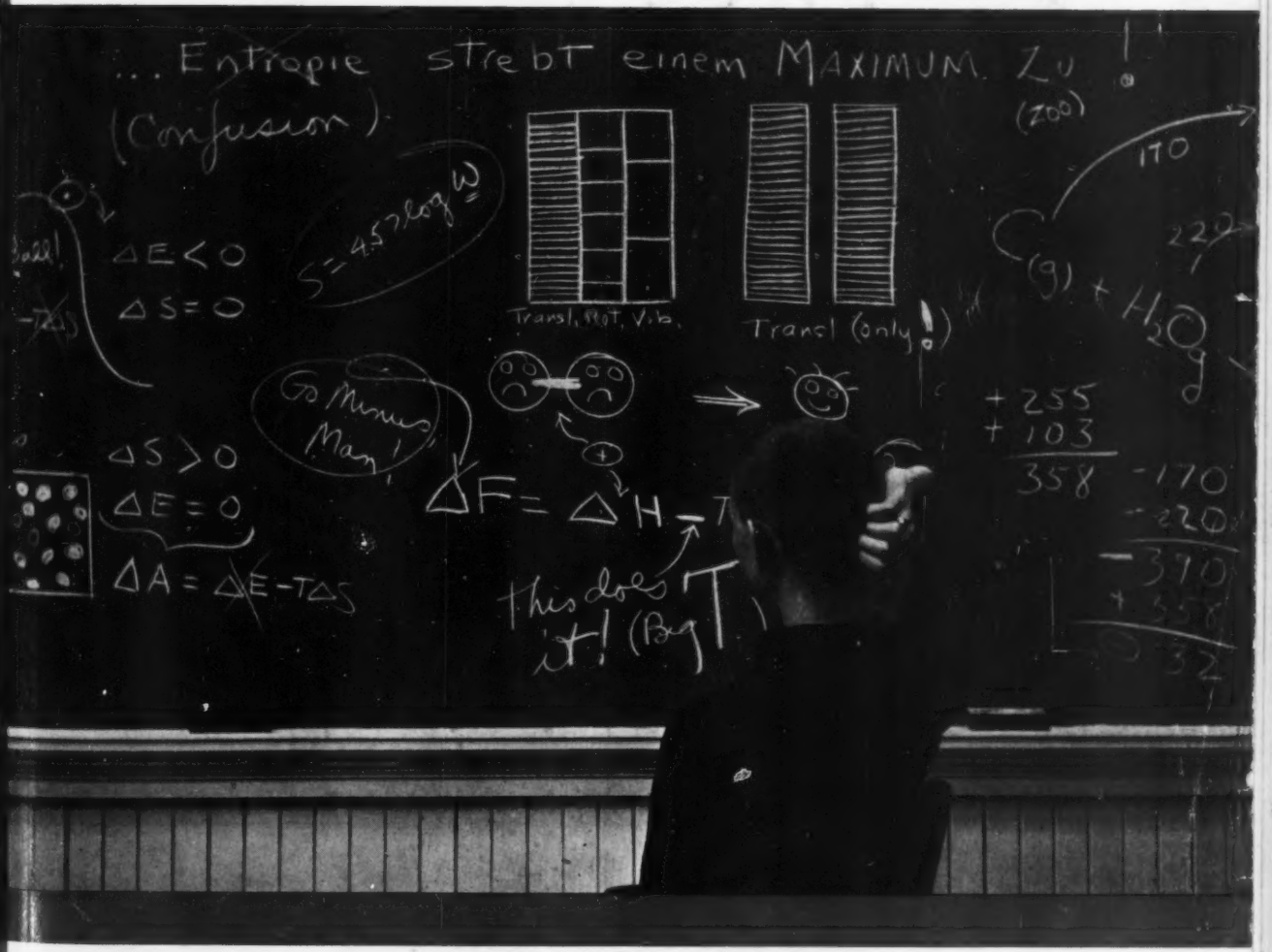
CHEMISTRY HALL LIBRARY

JULY 1961

JOURNAL OF Chemical Education

OHIO STATE UNIVERSITY
JUL 14 1961
LIBRARY

Published by the DIVISION OF CHEMICAL EDUCATION OF THE AMERICAN CHEMICAL SOCIETY

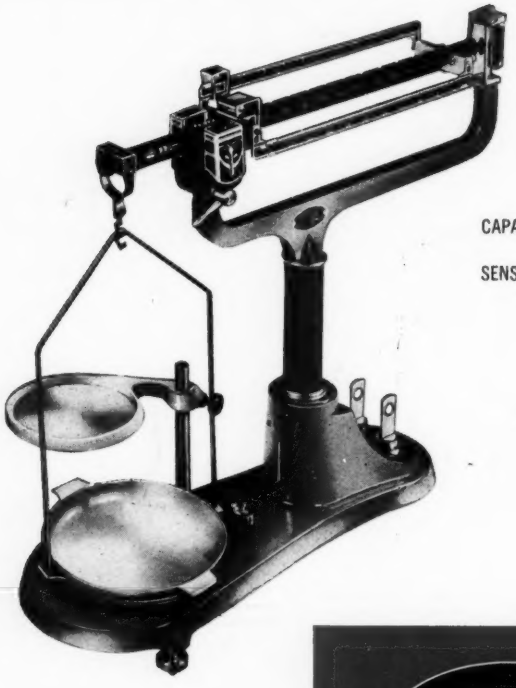


Will a Reaction Occur? . . . page 334

Salting-Out Chromatography . . . 338; Pesticides . . . 370

Radioisotope Experiments . . . 344-352

NOW...TWO MODELS...TWO CAPACITIES...FITS EVERY NEED



CAPACITY 311 Gram
SENSITIVITY .01 Gram

THE POPULAR

Cent O Gram

An unbeatable balance for general laboratory weighings, specific gravity work, and preweighing, the CENT-O-GRAM is an accepted pace setter in its field.

As well as being portable, this balance is adaptable for use in many fields.

The 311 gram capacity is higher than any balance of its type through use of two 100 gram self stored attachment weights.

Comes equipped with stainless steel bows, pan (3-3/4" dia. x 1/2" deep) and specific gravity platform.

OHAUS

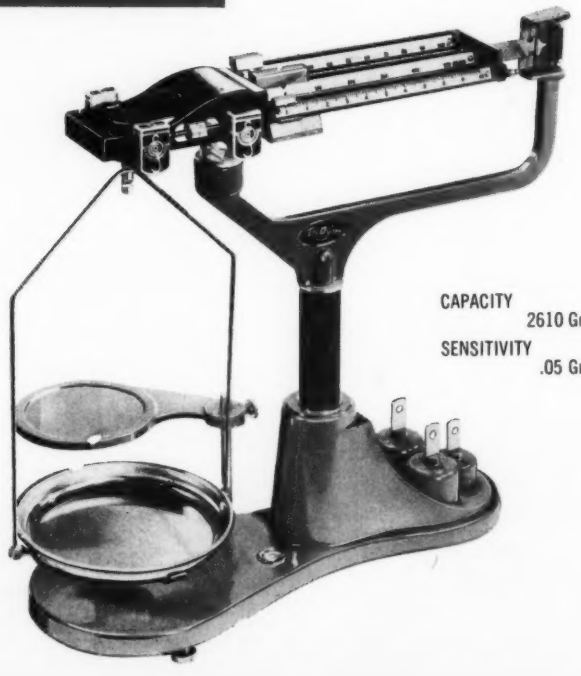
THE ALL NEW

Dec O Gram

This latest OHAUS overhead triple beam balance has a capacity of 2610 gram.

Such other familiar OHAUS features as sturdy box end beam, sliding type poise with center indicating panel, self aligning bearings, self storing attachment weights and specific gravity platform, all add up to fast sensitive high capacity performance.

Available in two models... the Model 3600 (metric) and Model 3601 (avoirdupois).



CAPACITY 2610 Gram
SENSITIVITY .05 Gram

OHAUS SCALE CORPORATION
1050 COMMERCE AVENUE UNION, NEW JERSEY
DEPT. JCE

Thomas SAFETY STOPPERS

THOMAS HR-108 SAFETY STOPPERS are of bloomless, black, resilient, heat resisting composition, with low sulfur content and long life. Straight bore of the conventional stopper has been replaced by a fusiform bore with bevelled entrance. Internal diameter at center approximately twice that of a sealing band at either end. Offer the following advantages:

SAFETY—Glass tubes can be easily inserted and removed, *particularly by students*, with greater safety than with straight bore. Insertion is facilitated by the bevelled entrance of the bore, and the tube slides through only the two sealing bands.

LARGER TUBES—Fusiform bore permits insertion of larger tubes than is possible with straight bore. For example, tubes 6 to 11 mm can be inserted in sizes 5 to 9 incl.

SUPERIOR COMPOSITION—The stock contains *more than 70% of pure virgin gum*, possesses great elasticity, is free from surface sulfur and contains less than 0.75% free sulfur; no reclaimed rubber is used.

HEAT RESISTANT—Temperatures *up to 110°C* do not affect shape, size or structure.

LONG LIFE—Tests indicate useful life approximately *five times* that of common stoppers.

8807. Safety Stoppers, Thomas HR-108, as above described, one hole (fusiform bore).

Size Number	Approx. no. per lb.	Carton Contains	Per Dozen	Per Carton
00	170	168	1.24	15.81
0	111	108	1.27	10.36
1	97	96	1.38	10.02
2	74	72	1.48	8.07
3	55	60	1.67	7.60
4	44	48	1.81	6.60
5	37	36	2.02	5.52
5½	31	36	2.18	5.94
6	27	30	2.33	5.29
6½	24	30	2.49	5.68
7	20	24	2.77	5.05
8	16	18	3.12	4.26
9	13	18	3.64	4.97

8808. Safety Stoppers, Thomas HR-108, as above described, but two hole.

Size Number	Approx. no. per lb.	Carton Contains	Per Dozen	Per Carton
00	169	168	1.34	17.04
0	110	108	1.37	11.23
1	95	96	1.48	10.78
2	74	72	1.58	8.65
3	55	60	1.79	8.15
4	46	48	1.87	6.79
5	38	36	2.04	5.58
5½	33	36	2.28	6.23
6	28	30	2.42	5.52
6½	25	30	2.56	5.81
7	20	24	2.83	5.15
8	17	18	3.16	4.31
9	14	18	3.60	4.92

5% discount from carton prices in lots of 6 cartons; 10% discount from carton prices in lots of 12 cartons
20% discount from carton prices in lots of 24 cartons; 30% discount from carton prices in lots of 48 cartons
one size, or assorted in carton units

For more detailed description, see pages 1066 to 1068 of our general catalog

QUALITY AND SERVICE
A.H.T.CO.
PHILA. U.S.A.
LABORATORY APPARATUS

ARTHUR H. THOMAS COMPANY

More and more laboratories rely on Thomas / *Laboratory Apparatus and Reagents*

VINE ST. AT 3RD • PHILADELPHIA 5, PA.

Wiley BOOKS

PHYSICAL CHEMISTRY OF MACROMOLECULES

By CHARLES TANFORD, *Duke University*. Beginning the treatment of each topic with an exposition of basic theory, Dr. Tanford covers the major areas of physical chemistry—molecular statistics, thermodynamics, light scattering transport processes and viscosity, electrostatics, x-ray diffraction, and equilibria and kinetics of reactions. All known varieties of macromolecules are treated and the discussion is supplemented by examples that make their uses clear. *1961. Approx. 752 pages. Prob. $18.00.*

ORGANIC REACTIONS — Volume 12

Editor-in-Chief: A. C. COPE, *Massachusetts Institute of Technology*. The five chapters in this latest addition to the series are: Cyclobutane Derivatives from Thermal Cycloaddition Reactions, The Preparation of Olefins by the Pyrolysis of Xanthates—The Chugaev Reaction, The Synthesis of Aliphatic and Alicyclic Nitro Compounds, Desulfurization with Raney Nickel, and Peptide Synthesis. *In Press.*

MEDICINAL CHEMISTRY — Volume V

Editor: WALTER H. HARTUNG, *Medical College of Virginia; Associate Editor:* ERNEST E. CAMPAIGNE, *Indiana University*. This is the most recent of the series of reviews prepared under the auspices of the Division of Medicinal Chemistry of the American Chemical Society. The contents includes: Anticonvulsant Drugs—by Warren J. Close and Marvin A. Spielman, and Bis(4-aminophenyl) Sulfone and Related Compounds in Tuberculosis and Leprosy—by Leonard Doub. *1961. Approx. 400 pages. Prob. $17.50.*

PROGRESS IN VERY HIGH PRESSURE RESEARCH

Edited by F. P. BUNDY, W. R. HIBBARD, *and* H. M. STRONG, *all of the Research Laboratory of the General Electric Company, Schenectady, N.Y.* This is a compendium of the papers and discussions presented at an International Conference on High Pressure Research held at Lake George, New York, June 13–14, 1960. The main topics of the conference were equipment and technique, structures of materials formed under high pressure, and behavior of matter under high pressure. *1961. 314 pages. $12.00.*

SOME RECENT DEVELOPMENTS IN THE CHEMISTRY OF PHOSPHATE ESTERS OF BIOLOGICAL INTEREST

By H. GOBIND KHORANA, *British Columbia Research Council; and Institute for Enzyme Research, University of Wisconsin*. Of special interest to chemists and biochemists working with phosphate esters, intermediary metabolism, and nucleic acids, this book reviews many of the developments in these fields, with special emphasis on recent synthetic work. *1961. Approx. 192 pages. In Press.*

RARE EARTHS

Edited by F. H. SPEDDING *and* A. H. DAANE, *both of Iowa State University, and Institute for Atomic Research, Ames Laboratory of the Atomic Energy Commission. With 29 other contributors*. A collection of papers presented at a symposium on rare earths and related metals held at the November 1959 meeting of the American Society of Metals. Reviews the present status in the rare-earth field, and covers rare-earth separation, preparation of the metals, and the properties of the metals and alloys. *1961. Approx. 640 pages. Prob. $14.75.*

IODIDE METALS AND METAL IODIDES

By ROBERT F. ROLSTEN, *Convair, A Division of General Dynamics. 1961. Approx. 496 pages. Prob. $17.50.*

MINERALS FOR THE CHEMICAL AND ALLIED INDUSTRIES

Second Edition. *By* SIDNEY JOHNSTONE, *Technical Consultant. In Press.*

Reserve your examination copies today.

John Wiley & Sons, Inc.

440 Park Avenue South *New York 16, N. Y.*

Published by the

DIVISION OF
CHEMICAL EDUCATION
OF THE
AMERICAN CHEMICAL
SOCIETY

OFFICERS

J. F. Baxter — Chairman
L. C. King — Chairman-elect
W. B. Cook — Secretary
W. G. Kessel — Treasurer
R. H. Maybury — Member-at-large Exec. Comm.

WILLIAM F. KIEFFER
Editor

Benjamin F. Gould
Advertising Mgr.

Mary Baker
Assistant to the Editor

BOARD OF PUBLICATION
J. F. Bunnett — J. F. Baxter
A. J. Harrison — W. B. Cook
S. S. Shaffer — W. G. Kessel

EDITORIAL BOARD
John L. Abernethy
University of Redlands
Redlands, California

Frederic B. Dutton
Michigan State University
East Lansing, Michigan

Robert D. Eddy
Tufts University
Medford, Massachusetts

Aaron J. Ihde
University of Wisconsin
Madison, Wisconsin

William G. Kessel
Indiana State Teachers College
Terre Haute, Indiana

S. Z. Lewin
New York University
New York 3, N. Y.

William F. Luder
Northeastern University
Boston, Massachusetts

John J. McKetta, Jr.
University of Texas
Austin, Texas

Karol J. Mysels
University of Southern California
Los Angeles, California

Ralph E. Oesper
University of Cincinnati
Cincinnati, Ohio

James M. Pappenhagen
Kenyon College
Gambier, Ohio

BUSINESS & PUBLICATION
20th and Northampton Streets
Easton, Pennsylvania

EDITORIAL OFFICE
The College of Wooster
Wooster, Ohio

ADVERTISING OFFICE
500 Fifth Avenue
New York 36, N. Y

JOURNAL OF Chemical Education

JULY 1961
Vol. 38 / No. 7

334 How Can You Tell Whether a Reaction Will Occur? *George E. MacWood and Frank E. Verhoek*

338 Salting-Out Chromatography: A Review, *William Rieman III*

344 Incorporating Radioisotope Techniques into the Chemistry Curriculum, *Norman S. Radin*

348 Ion Exchange-Radiochemical Experiment, *Joseph F. Mucci, Dorothy E. Spiegel, and Robert L. Stearns*

350 Radioisotope Demonstration of Common Ion Effect on Solubility, *E. Roig, I. G. Rieckehoff, C. S. Russo, and J. D. Curet*

352 Convenient Radioactivity Sources, *D. J. Carswell*

353 The Basis for a New Conception of an Electrode Potential: Escaping Tendency of Electrons in the Electrode of Electrode Systems at Equilibrium, *J. B. Ramsey*

357 Surface Area of Activated Charcoal by Langmuir Adsorption Isotherm, *Boleslaw Ludwik Dunicz*

358 The Turbidimetric Determination of Lead, *Gerald Perkins, Jr., J. W. Wimberley, J. F. Lamb, and L. E. Maurer*

361 An Inexpensive Coulometer for Titrations with Externally Generated Reagents, *William F. Head, Jr., and Max M. Marsh*

363 Revised Teaching of Biochemistry, *Howard M. Myers*

365 Is There an Alternative to pH? *Francis E. Crane, Jr.*

367 Chemistry Accidents in High School, *Robert D. Macomber*

369 Division of Chemical Education: From the Chairman, *John F. Baxter*

370 Proceedings of the California Association of Chemistry Teachers: Pesticide Residue Control under the Food, Drug, and Cosmetic Act, *Curtis R. Joiner*

375 Report of the New England Association of Chemistry Teachers: A Systematic Way to Avoid Le Chatelier's Principle in Chemical Reactions, *Lewis Katz*

Features

333 Editorially Speaking

A483 Out of the Editor's Basket

378 Letters

379 Book Reviews

A506 Advertisers' Index

A491 Chem. Ed. Tested Demonstration, *Frederic B. Dutton*

A457 Chemical Instrumentation, Nuclear Radiation Electronic Gear *S. Z. Lewin*

A501 Chemical Projects, *Jay A. Young and John K. Taylor*

Subscription Price: Domestic $4.00 per year; Canada $4.50; other countries $5.00. Issued monthly. Single copies of issues in current year, 60¢ each; all other single copies, $1.25. Remittances and orders for subscriptions should be sent to Business & Publication Office, 20th and Northampton Streets, Easton, Pa. Foreign remittances must be accompanied by International Money Order.

No claims for copies of journals lost in the mails can be allowed unless such claims are received within sixty (60) days of the date of issue and no claims can be allowed for issues lost as a result of insufficient notice of change of address. Manuscripts for publication should be directed to the editor. Prospective authors are urged to avoid diffuse writing and to observe the forms outlined in our Notice to Authors as it appears opposite page 663 of the Dec. 1960 issue. Second-class mail privileges authorized at Easton, Pa. Accepted for mailing at special rate of postage provided for in Section 1103, Act of Oct. 3, 1917, authorized Jan. 31, 1924.

The JOURNAL OF CHEMICAL EDUCATION is the official organ of the Division of Chemical Education and incorporates the Report of the New England Association of Chemistry Teachers, and the Proceedings of the Pacific Southwest Association of Chemistry Teachers. It is indexed in the Education Index, Industrial Arts Index, and, in part, in the Quarterly Cumulative Index Medicus.

© Copyright, 1961, by Division of Chemical Education, American Chemical Society

The SARGENT Model XV
RECORDING POLAROGRAPH®

offers you—

- **FULL 10 INCH CHART**
- **1/10% ACCURACY OF MEASUREMENT**
- **TEN STANDARDIZED POLARIZING RANGES**

This new Sargent POLAROGRAPH gives you a large 250 mm (10 inches) chart and the highest accuracy and current sensitivity at the lowest price of any pen writing polarographic instrument on the market.

It offers you optimum specifications based on over twenty years of leadership in design, manufacture and service in this specialized field of analysis.

The polarographic method is capable of reproducibility to 1/10% and analytical accuracy to ½%. To make use of this facility, the instrument must be accurate to 1/10% and chart space must be provided for recording large steps to achieve measuring precision. We strongly advise against the purchase of any polarographic instrument using miniature (5 inch) charts and low gain balancing systems in the 1% order of precision.

This Model XV is adaptable to 10^{-6} M determinations with the S-29315 Micro Range Extender.

®Registered Trade Mark (Pat. No. 2,931,964)

Current Ranges:	19, from .003 to 1.0 μA/mm.
Polarizing Ranges, volts:	0 to −1; −1 to −2; −2 to −3; −3 to −4; +.5 to −5; 0 to −2; −2 to −4, +1 to −1; 0 to −3; +1.5 to −1.5.
Balancing Speed:	standard, 10 seconds; 1 second or 4 seconds optional.
Bridge Drive:	synchronous, continuous repeating, reversible; rotation time, 10 minutes.
Chart Scale:	current axis, 250 mm; voltage axis, 10 inches equals one bridge revolution.
Current Accuracy:	1/10%
Voltage Accuracy:	¼%
Chart Drive:	synchronous, 1 inch per minute standard; other speeds optional.
Writing Plate:	10½ x 12½ inches; angle of slope, 30°.
Standardization:	manual against internal cadmium sulfate standard cell for both current and voltage.
Damping:	RC, four stage.
Pen:	ball point; Leroy type optional.
Suppression:	zero displacement control, mercury cell powered, 6 times chart width, upscale or downscale.
Potentiometric Range:	2.5 millivolts, usable as general potentiometric recorder.
Finish:	case, enameled steel; panels, anodized aluminum; writing plate, polished stainless steel; knobs and dials, chromium plated and buffed.
Dimensions:	23 x 17 x 10.
Net Weight:	65 pounds.

Catalog number **S-29310** with accessories and supplies. . . . **$1585.00**

For complete information write for Sargent Bulletin P

SARGENT *SCIENTIFIC LABORATORY INSTRUMENTS • APPARATUS • SUPPLIES • CHEMICALS*

E. H. SARGENT & CO., 4647 W. FOSTER, CHICAGO 30, ILLINOIS
DETROIT 4, MICH. • DALLAS 35, TEXAS • BIRMINGHAM 4, ALA. • SPRINGFIELD, N. J.

Chemical Instrumentation

S. Z. LEWIN, New York University, Washington Square, New York 3, N. Y.

. . . a Chem Ed feature

This series of articles presents a survey of the basic principles, characteristics, and limitations of those instruments which find important applications in chemical work. The emphasis is on commercially available equipment, and approximate prices are quoted to show the order of magnitude of cost of the various types of design and construction.

13. Nuclear Radiation Electronic Gear (Concluded)

Nuclear-Chicago Corp.

An extensive line of nuclear radiation instrumentation, as well as radioactive sources and standards, labeled compounds, detectors, and training kits, is manufactured by the Nuclear-Chicago Corporation, Des Plaines, Illinois. This company's instruments run the gamut from small survey meters to a subcritical training reactor, and are currently in widespread use.

Survey Meters. The line of portable, battery-powered, radiation survey instruments includes a count-rate meter employing Geiger-Müller tube detectors (Model 2612M for general beta-gamma survey work, with a Model D50 thin glass-wall G.M. tube, $255; Model 2612P for also surveying for alphas and weak betas, with a Model D35 thin mica end-window tube, $295). The circuit uses two hearing-aid type vacuum tubes, a 25-microampere read-out meter, crystal earphones, and a 900-v stabilized audio oscilliator high-voltage supply for the G.M. tube. The battery complement consists of two 1.5-v flashlight type cells, and two 67.5-volt portable radio type cells. The ranges are 0.2, 2.0, and 20 mr/hr full scale, and the accuracy is ±10%. A calibrated reference source is mounted on the instrument case, and the output signal can be recalibrated as often as desired by means of a screwdriver adjustment accessible to the user.

This basic instrument is also available in a modified form designed for use with special detector probes for alpha and neutron survey work (Model 2112P, with Model AP4 alpha probe, $445; Model 2112N, with Model DN3 neutron probe, $670). The count-rate meter circuit is modified to adjust the time constants to the characteristics of the probes, and a transistorized high-voltage supply based upon three 1.3-v mercury batteries and two 67-v batteries is employed to provide the probe voltage.

The alpha probe consists of an unsealed air proportional chamber with an active area of 75 cm² and a window (of rubber hydrochloride, Aquadag-coated to minimize static charge effects) thickness of *ca.* 0.7 mg/cm²; mounted on the back of this chamber is a transistor amplifier with a gain of 100, which raises the signal due to the alpha pulses from its initial value of 0.0025 v to the 0.25 v necessary to trigger the count-rate meter circuit. This probe will detect as little as 2 alphas/cm²/min.

The neutron probe contains a brass-wall counter, $^5/_8$-in. in diameter and 3.5-in. in active length, filled with B-10 enriched BF_3. When thermal neutrons interact with B-10 nuclei, the following transformation occurs:

$$n + \text{B-10} \rightarrow \text{Li-7} + \alpha$$

The alphas generated in the probe chamber produce an ionization current, and are detected by the type of circuitry described above for the alpha probe. For the detection of fast neutrons, the probe is supplied with a removable, 1-in. thick, paraffin shield with an outer liner of cadmium. When this moderator is in place, slow neutrons (i.e., those with energies below the cadmium resonance at 0.176 ev) are absorbed by the cadmium liner; the more energetic neutrons pass through this shield and enter the paraffin moderator, where they are slowed down to thermal energies before entering the counter tube. The neutron probe is insensitive to gamma radiation intensities as great as 50 r/hr.

A survey instrument is also available which contains two neutron probes, one for thermal neutrons and a second, in a wax block surrounded by cadmium, for fast neutrons (Model 2715 Nemo, $1350). The range is 10 to 10^4 neutrons/cm²/sec, and is read-out on a single, logarithmic meter scale.

Survey instruments for the monitoring of fairly high field intensities and which are designed with a pistol grip, so that the unit can be aimed at the area to be surveyed as a gun is aimed at a target, are commonly called "*Cutie-Pie*" instruments. Nuclear-Chicago's Cutie-Pie survey meters consist of a main body containing the power supply, amplifier, and read-out meter, and a detachable ionization chamber unit. An example of this type of instrument is shown in Figure 34. The ionization current generated by the radiation field is preamplified in a feedback-stabilized electrometer circuit which is sealed into the ionization chamber housing, and further amplified in the main body of the instrument. Model 2586 ($365) is supplied with a 500-cc cylindrical ionization chamber, and is suitable for measuring beta or gamma radiation up to 2500 mr/hr. In order to measure higher intensities with the same circuitry, it is necessary to reduce the volume of the ionization chamber, so that the detector current remains within the limits imposed by the characteristics of the electrometer tube. Thus, Model 2586P ($395) is supplied with a 5-cc ionization chamber, and it can be used for radiation intensities up to 250 r/hr. Also available is the Model 2586S ($475) which is supplied with two interchangeable chambers; one gives instantaneous dose rate information, and the other provides integrated (i.e., total accumulated) dose measurements.

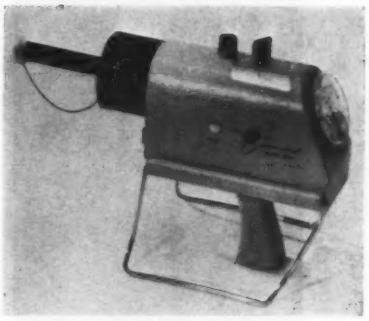


Figure 34. A "Cutie-Pie" gun-type portable survey meter (Model 2586 of Nuclear-Chicago). The sensor is a detachable cylindrical ionization chamber with sealed-in electrometer preamplifier. The body of the instrument contains the power supply, amplifier, read-out meter, and pistol grip.

Ratemeters. A ratemeter (or, count-rate meter) does not differ in principle from a survey meter; it is common practice among instrument manufacturers to employ the designation "survey meter" for instruments which are portable and of limited accuracy (probable error ±10 %, or more), and to designate as "ratemeters" the nonportable, more elaborate instruments intended for use at the laboratory bench. Such ratemeters are widely used for monitoring the radiation level at a working area, for checking radioactive contamination on hands or apparatus, for mapping out the distribution of radioactivity in a region, and for conducting rapid, moderate-precision assays of ores, solutions, and other samples.

The Nuclear-Chicago Model 1613A "Classmaster" Radioactivity Demonstrator ($195) is an inexpensive ratemeter with a number of accessories specifically designed for use in classroom demonstrations of some of the properties of beta and gamma radiation. The radiation intensity being sensed by the Geiger-Müller tube is presented as a meter deflection; to enhance the utility of this instrument for the classroom, a neon lamp mounted on the front panel flashes at a rate proportional to the rate of pulsing of the G.M.

tube, and thus provides a second form of visual read-out. Simultaneously, a built-in speaker produces audible clicks at the

(*Continued on page A460*)

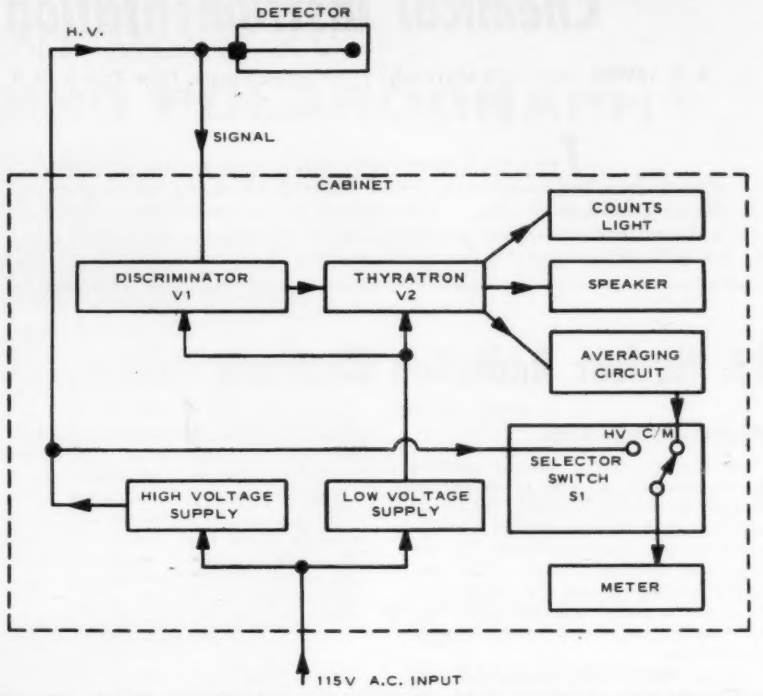


Figure 35. Block diagram of the circuitry contained in the Nuclear-Chicago Model 1613A Classmaster radioactivity monitor. The discriminator passes 0.25 volt pulses to the thyratron tube amplifier, which presents reshaped pulses for three different simultaneous types of read-out. The meter can read either counts per minute or voltage, depending upon the position of the selector switch.

THE NEXT TIME YOU ORDER ORGANICS

We hope, the next time you order organics, you'll specify MC&B. We think there are some pretty fair advantages in specifying our chemicals. For example—

Convenience—the best Distributor Network in the business

Dependable Purity—Each lot checked to maintain purity

Complete Line—Over 4400 laboratory chemicals. Write for Catalog.

Will you specify MC&B the next time? We'll appreciate the business, and so will our good distributors.

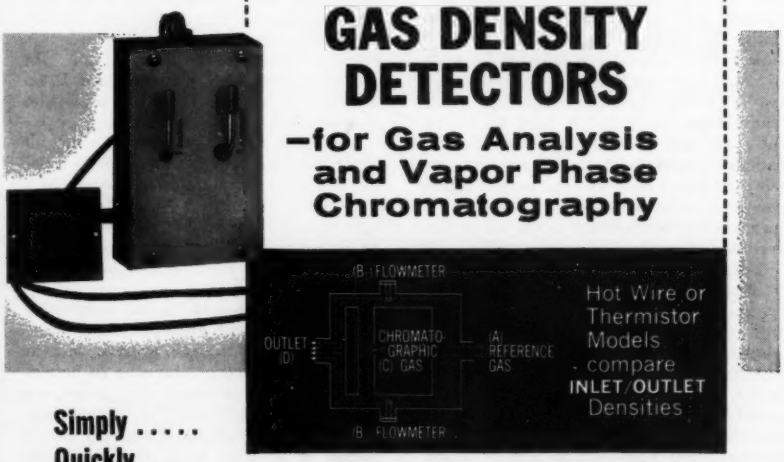
M C&B

Matheson Coleman & Bell Division of The Matheson Company, Norwood (Cincinnati), Ohio; East Rutherford, New Jersey

GOW-MAC offers two new

GAS DENSITY DETECTORS

—for Gas Analysis and Vapor Phase Chromatography



Simply .....
Quickly.....
Accurately..
Reliably ....

SIMPLY with Nitrogen or Argon—

- Inert Carrier Gas
- Easily-built Gas Train
- Standard Electrical Circuitry (as for thermal conductivity)
- Normal Recorder Readout
- Quantitative Measurement

BUT—

- No Calibration to Standard Sample

GOW-MAC INSTRUMENT COMPANY

100 KINGS ROAD, MADISON, N. J., U. S. A. • Telephone: FRontier 7-3450

GAS ANALYSIS INSTRUMENTS SINCE 1935

. . . AND A PINCH OF METHYL IODIDE C^{14}

If following a "recipe" was the only talent needed to create good *radiochemicals*, almost anyone could prepare them. But it takes much, much more.

Tracerlab was the *first* company to undertake the synthesis of radiochemicals for research use. That means a head start on everyone else in radiochemical research, control, purity, packaging, storing and stocking. Our advanced methods of manufacture and control insure radiochemicals of absolute uniformity and purity. More important is the *personalized service* we offer. Many of you have been visited by a Tracerlab radiochemist interested in your problems; others have called our labs to talk personally with the chemists involved in preparing your compound. Your requests to Tracerlab receive the special attention of qualified interested people.

For radiochemicals from stock (within 24 hours by air) or special compounds made to your specifications, call Tracerlab, TWinbrook 4-6600, extension 363. Your orders, large or small, will receive prompt, *personal attention*. Ask for the Tracerlab Radiochemical Catalog today.

Tracerlab Tracerlab KELEKET

TRACERLAB, INC., 1601 Trapelo Rd., Waltham 54, Massachusetts

NEW! **DOPA-2,3-H^3, DOPAMINE-β-H^3, D-GLUCOSE-1-C^{14}, D-GLUCOSE-2-C^{14} D-GLUCOSE-6-C^{14}**

a RATEMETER TO FIT YOUR BUDGET from LIONEL*

$175 F.O.B Brooklyn Plant Price Includes Probe and Detector

The new transisterized Type 457 radioactivity ratemeter will fit the most modest school or university budget and will fill your radiological counting needs with years of accurate trouble-free service.

- Transistorized—No warm-up time.
- Adjustable Power Supply (500 V to 1200 V).
- Large 4½ inch meter face indicates count rate . . . has dual range: 0-1500 CPM; 0-15,000 CPM.
- Loudspeaker for aural monitoring with volume control.
- Neon flasher for visual monitoring.
- External jack for meters or recorders for demonstrations, etc.
- The Anton/Lionel 114/6993 thin-wall, stainless steel halogen quenched counter tube will withstand the most severe laboratory or student abuse. Its life is unaffected by extended operation and it cannot be damaged by overvoltage.
- The Type 457 was designed to perform all experiments and demonstrations such as those listed in "Teaching with Radioisotopes prepared by the U.S. Atomic Energy Commission."

LIONEL ELECTRONIC LABORATORIES Division of the Lionel Corporation

*FORMERLY ANTON ELECTRONIC LABORATORIES, INC. / 1226 FLUSHING AVE., B'KLYN 37, N. Y.

same pulsing rate to provide a third form of read-out. A block diagram of the electronic circuitry of this instrument is given is given in Figure 35.

The Model 1619A "Labitron" ($325) is a more precise instrument designed primarily for monitoring work. A high-voltage supply that is continuously variable from 600 v to 2150 v is provided, and the same meter that serves for read-out of the counting rate can be employed by means of a selector switch to measure the voltage that is being applied to the G.M. tube. The 0.25-v pulses from the G.M. tube are reshaped in a flip-flop (univibrator) circuit and fed to the integrating (capacitor storage) circuit. A loudspeaker with adjustable volume control provides a simultaneous aural indication of radiation intensity. A connector is provided at the rear of the chassis for the attachment of any 1-milliampere recorder, so that a continuous record of radiation intensity can be obtained as a function of time or of location of the probe.

The Model 1620BS Analytical Count Rate Meter ($675) is intended to provide the maximum precision possible with a ratemeter read-out, i.e., to keep all errors and nonlinearities below the precision of reading of the output meter. The main problem in constructing a precision ratemeter lies in the necessity of insuring that the same charge is fed to the integrating capacitor for every primary pulse, regardless of the size, shape or duration of the pulse, and independent of variations in the characteristics of components and vacuum tubes, or of fluctuations in the supply voltage. The degree of sophistication of the circuitry needed to achieve this result is illustrated by the block diagram of the Model 1620 given in Figure 36.

The lower half of the diagram represents the power supply. When the instrument is turned on, a 30-sec delay switch (*K-1*) prevents the high-voltage from being applied to the high-voltage rectifier until any transient overshoots have died away and the tubes have warmed up. The upper half of the diagram shows the ratemeter circuits. The input pulses, which must exceed a minimum voltage that is generally chosen as 0.25 v because this is the size of the pulse usually produced in a G.M. tube detector, but which can be set for any value in the range 0.1 to 1.0 v, are fed into amplifier and pulse-shaping circuits, and finally to the storage (integrating) circuit. The voltage built up on the storage capacitor is amplified by a dc feedback amplifier (*V-6*), in which the output is fed back to the input through the time constant, *RC*-delay, circuit (not shown). The amplifier output is read out by means of a vacuum tube voltmeter (*VTVM*), and simultaneously by a loudspeaker.

The basic circuit error in this instrument is less than $\pm 0.25\%$; the over-all error is determined by the D'Arsonval meter movement and is about $\pm 2\%$ of the meter reading. The loudspeaker system which is incorporated for aural monitoring has the unique feature of giving a tone that varies in pitch in proportion to the counting rate. The frequency of the oscillator, *V-8*, is controlled by the *VTVM* output. A distinct change can be detected aurally

(*Continued on page A462*)

COLEMAN

New filters isolate Mg, Li for rapid flame analysis

Magnesium from 5 to 4,000 ppm; lithium from 0.0097 to 970 ppm—measurements in these concentrations are quick and easy with two new spectral filters now available for use with the Coleman Flame Photometer.

Another accessory, the **Autoflow Sample Handling System, actually triples analytical speed**—by providing direct feed of sample to atomizer burner and automatic and instantaneous removal of unused sample.

With its analytical scope now encompassing five important metallic elements (Na, Ca, K, Mg, Li) . . . with its unequalled speed and convenience of analysis . . . the Coleman Flame Photometer is a time and money saver for **any** laboratory charged with a heavy analytical work load. Simple and dependable, it requires no water connections, no special fuel gas, and no specially-trained operators.

The advantages of flame analysis over wet chemistry methods have long been established—improved precision in analysis of these elements in higher concentrations; accurate trace analysis in extremely low concentrations; major savings in time, effort, chemicals and laboratory space.

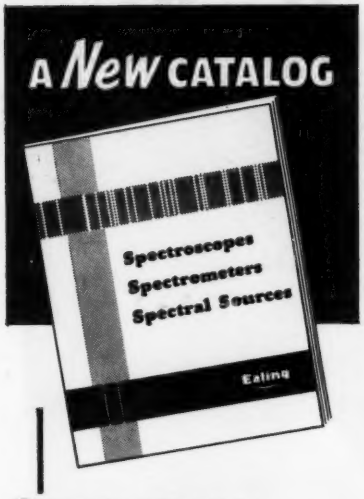
Find out about the special advantages of **Coleman** flame analysis.

Ask for these publications:

BB-242A—Coleman Flame Photometer;
BB-265—Autoflow Sample Handling System;
BT-169—Flame Photometric Determination of Magnesium;
BT-174—Flame Photometric Determination of Lithium.

Order and simplification are the first steps toward mastery of any science

COLEMAN INSTRUMENTS, INC., MAYWOOD, ILLINOIS



Spectroscopes

The most complete list offered.
Hand - Diffraction - Prism
Wavelength Prism
Microspectroscope
Bunsen Kirchoff.

Spectrometers

Featuring instruments using the spectrum reversion technique developed by Hartridge.
Wavelength Diffraction
Direct Reading Reversion
Clinical Hartridge Reversion
Student - Advanced.

Spectral Sources

Osram Spectral Lamps.
New
Philips Spectral lamps.

THIS NEW CATALOG SENT FREE ON REQUEST FROM:

THE **Ealing** CORPORATION

33 University Road,
Cambridge 38, Massachusetts

Telephone : KIrkland 7-5760
Teletype : Cambridge 62
Cable Address : Ealing

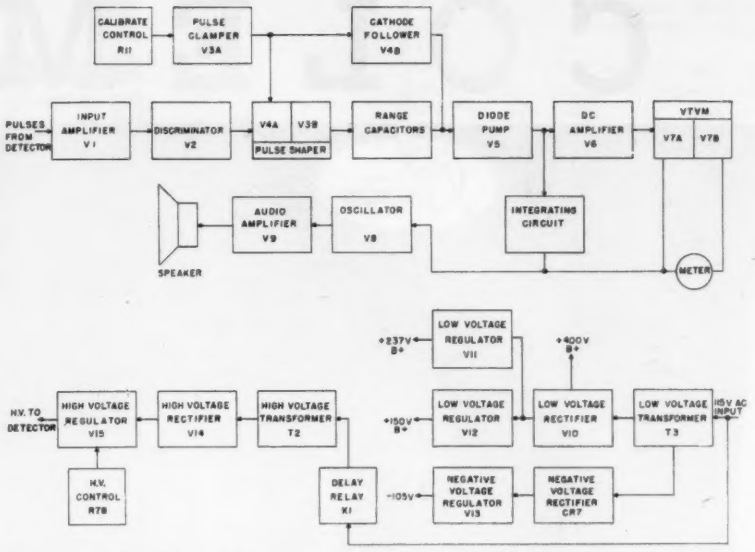


Figure 36. Block diagram of the circuitry of the Nuclear-Chicago Model 1620 Analytical Count Rate Meter. Lower half of diagram shows the power supply sections; upper half shows the amplifier, pulse-shaper, and read-out circuitry.

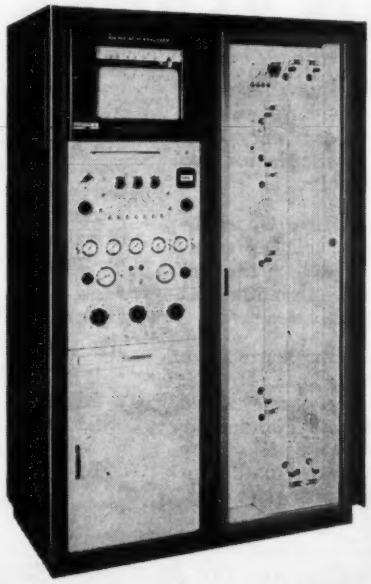
for very small changes in the counting rate. Connections are also provided for attaching this ratemeter output to either a 1-milliampere direct deflection recorder, or a 10-millivolt potentiometer recorder.

The most recent developments in this line of ratemeters comprise two units that are part of this company's so-called "Logic" series of instruments; this series consists of a number of modular units which can be assembled into a variety of integrated counting and spectrometry systems. The Model 8350 Linear Ratemeter ($1085) is a precision instrument which will accept inputs from any G.M., porportional, or scintillation detector. The ranges are from 300 up to 10^7 cpm

(Continued on page A464)

New PHOENIX AMINO ACID ANALYZER

MODEL K-8000



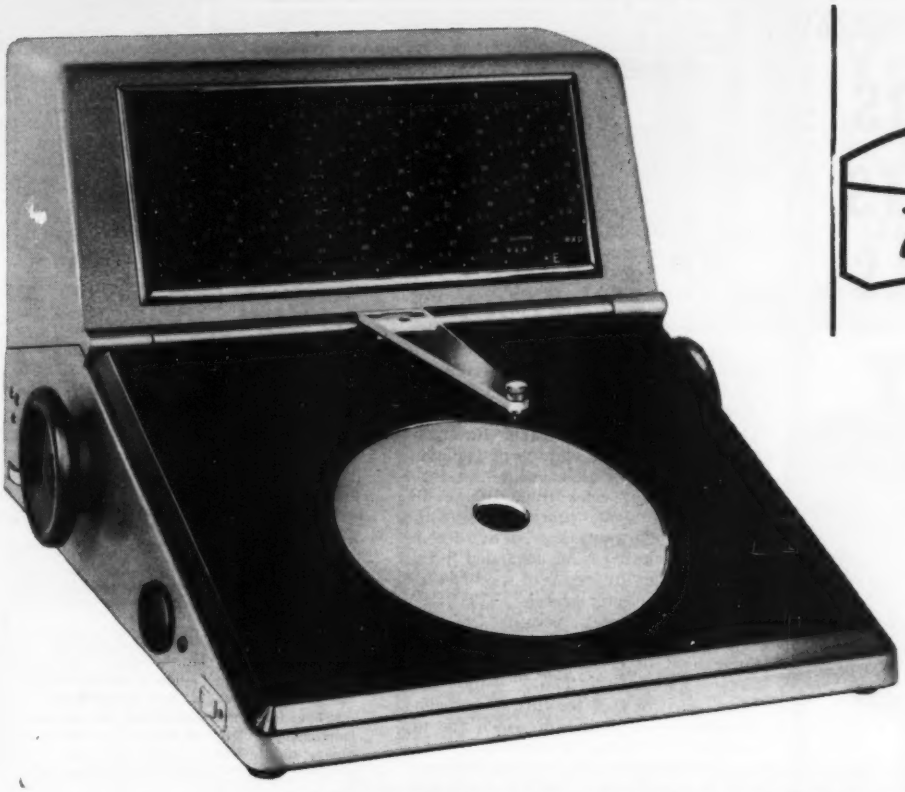
Automatic Analysis of Amino Compounds in

- Protein Hydrolysates
- Protein free plasma and other
- Physiological fluids
- Tissue extracts
- Hydroponic solutions
- Foods
- Culture media
- Pharmaceuticals
- Adaptable to Phoenix Stream Splitting System 5500

Sensitivity: 0.1 to 3.0 micromoles of amino acid with a precision of 100 ± 3%. Useful results at even lower levels.

PPI

PHOENIX PRECISION INSTRUMENT COMPANY
3803-05 NORTH FIFTH ST., PHILADELPHIA 40, PENNSYLVANIA



CARL ZEISS

WEST GERMANY

PARTICLE SIZE ANALYZER

After Endter

An entirely new method of analyzing and counting particles according to their size

By means of an ingenious diaphragm which activates 48 different counters, the instrument, using enlarged photographs of the particles, permits the counting and classifying of approximately 1,000 particles in less than 15 minutes.

Particularly valuable for analyzing photographs of particles taken with the Electron Microscope.

Instrument is approximately the size and weight of a typewriter. Moderately priced.

Write for literature which gives complete details

CARL ZEISS, INC.

485 FIFTH AVENUE, NEW YORK 17, N. Y.

COMPLETE SERVICE FACILITIES

OUTSTIRS
OUTLASTS
OUTSELLS

LOW COST $25.25

HIGH TORQUE Stirs thickest liquids. Won't stall, won't burn out.

EXTRA LIFE MOTOR Not a stock motor, but special heavy duty Waco motor. Many labs operate this stirrer 24 hours a day, 7 days a week, month after month.

BUILT IN FAN Cools motor, permits continuous use. Outlasts others, saves replacement.

SAFE, NON-SPARKING Induction type motor is safe for stirring flammables.

2 SPEEDS With one 300 and one 600 R.P.M. ¼" shaft. These speeds cover the vast majority of stirring needs.

Order Today on Our Guarantee

E-10235 Waco stirrer with brass mounting rod and 6 foot cord.....$25.25

E-10235-1 Stirrer chuck for Waco stirrer for ¼" stirring rods.....$ 1.65

Catalog 38 Stirrers

Write for free Catalog No. E-3, describing 38 different stirrers for every stirring job.

WILKENS-ANDERSON CO.
4525 W. DIVISION ST. CHICAGO 51, ILL.

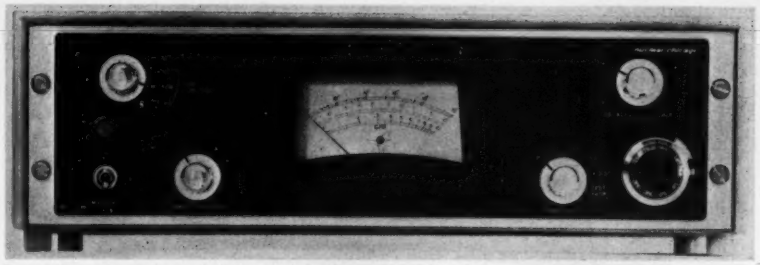


Figure 37. Control panel of the Nuclear-Chicago Model 8360 Logarithmic Ratemeter.

full-scale, with time constants from 0.2 to 100 sec. An "integrate" position on the time constant selector switch permits the counting rate to be integrated, as, e.g., over a spot on a paper chromatogram. The Model 8360 Logarithmic Ratemeter ($1160) provides the features of displaying on a logarithmic meter scale the entire range of count rates from 10^2 to 10^7. Figure 37 shows the control panel of this ratemeter. Any one, three, or five decades of the count rate can be expanded to full-scale deflection by means of the "Decades Full Scale" selector switch. The "CPM Suppressed" switch permits 10^2, 10^3, 10^4, 10^5, or 10^6 cpm to be selected as the lower limit of count rate shown on the meter movement. The "+100 Volt Disc." control is a ten-turn variable potentiometer by means of which the discriminator level can be set with precision to any voltage between +5 and +100 v.

Scalers. This manufacturer produces a variety of scalers that include binary, binary-decimal, glow transfer, and beam-switching scaling stages. The instruments in current production are sum-

(*Continued on page A467*)

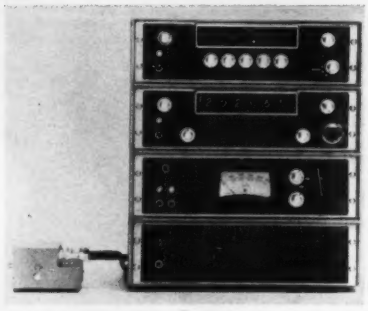


Figure 38. Precision general-purpose radioactivity measuring instrumentation of Nuclear-Chicago featuring in-line numerical read-out. The chassis shown are, from the bottom: a preamplifier (the small unit at the left), a base unit (containing cooling fan blowers), a high voltage power supply unit, a scaler unit, and a timer unit.

DISC ELECTROPHORESIS

For Research • Clinic • Classroom

TRIAL KITS AVAILABLE FOR JULY SHIPMENT

Revolutionary breakthrough in protein separation, using new, specially processed polyacrylamide gel. Routinely separates 20-30 proteins in human serum. 100 times more sensitive than starch gel.

Reproducible • Fast • Easy to Use

Thoroughly proven in blood serum, plasma, plant and animal tissue (protein and enzymes) body fluids and egg white. Try this remarkable new technique now on your own samples.

TRIAL KIT: complete set of chemicals for 100 experiments, equipment, accessories, without power supply ..... **$38.**

(Optional DC power supply (20ma at 150 V) ..... **$18.**

f.o.b. Bethesda, Md.

Order Now For Prompt Delivery

CANALCO

CANAL INDUSTRIAL CORP.
Dept. C7 4935 Cordell Avenue
Bethesda 14, Maryland

PRECISION SCIENTIFIC CO. PS

Yearly Review

Calendar of NEWLY INTRODUCED PRODUCTS 1960-1961

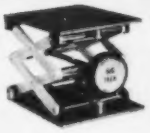
MAY 1960

New Heated Vacuum Dessicator

A versatile lab utility—dries faster, maintains samples at desired temperatures, evaporates solvent traces rapidly, does double duty as a vacuum oven—get Bulletin 608 for complete details.

AUGUST 1960

BIG JACK and LITTLE JACK



STURDY, DEPENDABLE LABORATORY JACKS

Big Jack raises or lowers heavy flasks, hot plates, baths, etc. up to 100 pounds—3 to 12 inches.
Little Jack, a smaller model of Big Jack designed to work with small objects—lifts or lowers up to 10 pounds—1½" to 5". Ideal for micro work. Write for Bulletin 611.

NOVEMBER 1960

Wet Test Meters

Designed to afford increased pressure range . . . from 0.3 inches water pressure to 15 PSI. Self serviced by easy removal of the back cover. Housing is of heavy cast aluminum with epoxy coated interior. Construction throughout assures longer life. Write for Bulletin No. 612.

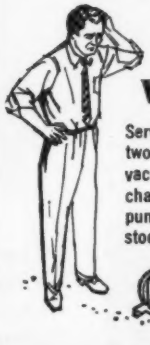
DECEMBER 1960

New Therm-O-Plate Hot Plates

Do you want to Heat?—Stir?—Shake? Need up to 800°F? Then depend on Therm-O-Plate line. Four types—eleven sizes—standard models, stirring, heating, shaking, heating and explosion proof models. Get full details—send for Bulletin 609.

JANUARY 1961

Unique Pump Exchange Program for Precision Vacuum Pumps



Service it yourself. Here are two single plans to reduce your vacuum pump problems. Interchangeable parts or rebuilt pumps always available from stock. Write for Bulletin 616.

FEBRUARY 1961

Micro Serological Bath

A truly versatile small bath—for micro work and exacting tests—occupies only ¼ square foot—has range up to 100°C—uniformity ±0.2°C or better. Weighs only 5 lbs. Has new universal rack for simultaneous use of various sizes and shapes of tubes, flasks and beakers—has micro tube rack for 6 to 12 mm. tubes. Write for Bulletin 613.

MARCH 1961

Constant Temperature Controlled Agitation Shaker Baths

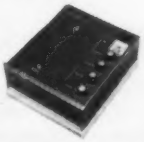
Complete new line—for Microbiological, Biochemical and Physio-Chemical studies. Variable speed control. Adjustable stroke length. Guaranteed temperature uniformity ±0.5°C. or better. Three sizes to meet all requirements. Write for Bulletin 614.

MORE COMING IN THE MONTHS AHEAD

NOW...CHRONOFRAC

A New... Fully Guaranteed... Professional Quality... GAS CHROMATOGRAPH

ONLY $250



A speedy reliable solution to routine gas and volatile liquid analysis problems... Quickly pays for itself in savings in time and material... Inexpensively makes gas chromatography available to everyone.

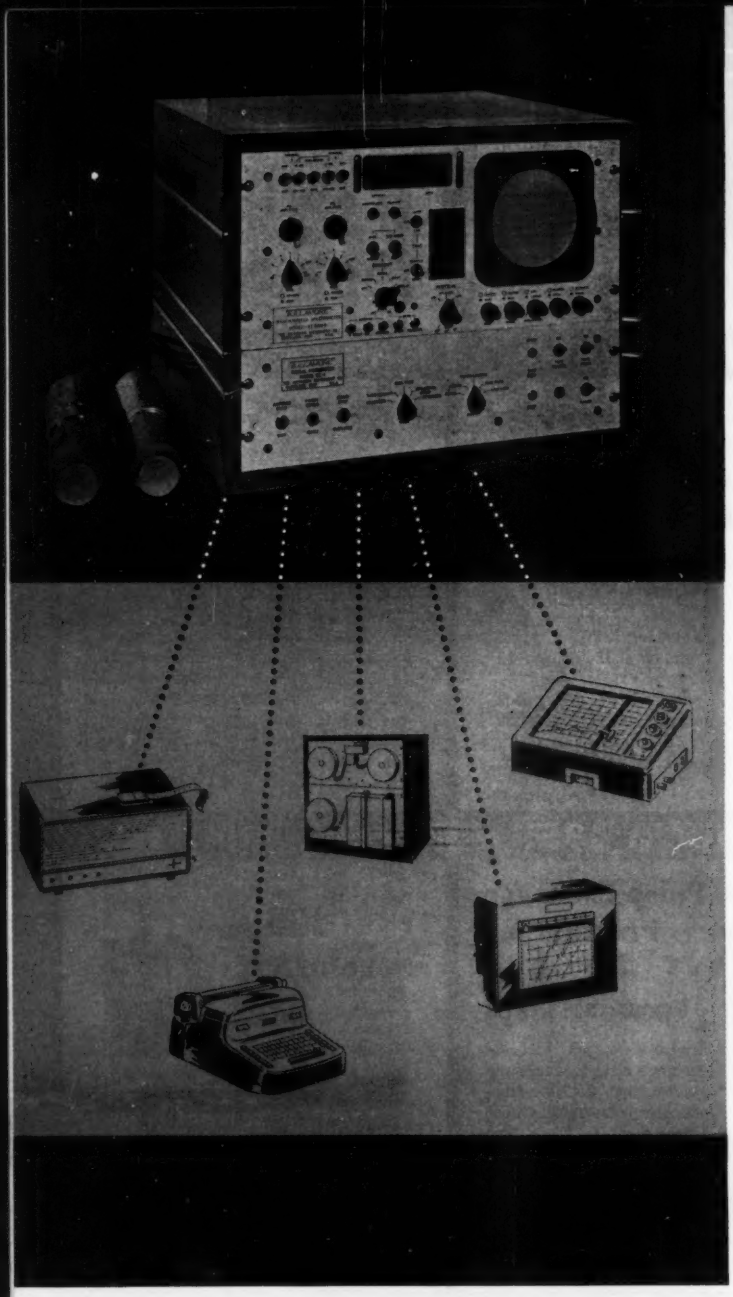
Ideal for quality control of any raw material or finished product with boiling point to 105°C. (and many up to 120°C.) ...Safeguards the quality of the product you sell...the products you buy. Simply installed and operated.

Since 1920 Precision Scientific Company has directed its efforts toward producing new instruments in keeping with the latest advancements in scientific technology.

PRECISION SCIENTIFIC CO. PS

3738 WEST CORTLAND STREET
CHICAGO 47, ILLINOIS

LOCAL OFFICES IN:
CHICAGO • CLEVELAND
HOUSTON • NEW YORK
PHILADELPHIA • SAN FRANCISCO



Now Building
MULTI-DIMENSIONAL ANALYZERS . . .

Victoreen

Victoreen, the first name in radiation measurement, is delivering the last word in multi-channel analyzers—the Tullamore-designed Model ST-200D

- 200 or 400 Channel ferrite core memory
- Dual input—Simultaneous data accumulation
- Subgrouping and bi-directional logic
- Parallel or serial readout—Wide selection of readout devices
- Visual display and readout—Linear, log or both simultaneously
- Simultaneous linear and log plot

A-4003A

. . . and
400 and 800 CHANNEL
(1-8 Inputs)
"M" SERIES

Service by
RCA SERVICE COMPANY
A Division of Radio Corporation of America

V I C T O R E E N

5806 HOUGH AVENUE • CLEVELAND 3, OHIO
EXPORT: 240 WEST 17TH ST. • NEW YORK 11, NEW YORK

Table 2. Nuclear-Chicago Scalers

Model	Type of scaling	Scale factor	Input sensitivity	Resolving time (microsec)	High voltage supply (v)	Price
161A	Binary	256	0.25 v	5	500–2500	$ 675
151A	Binary-Decimal	2 decades	0.25 v	5	500–2000	547
181B	Binary-Decimal	3 decades	0.25 v	1	400–3000	845
183B	Binary	256	0.25 v	1 or 5 by selector switch	500–2500	960
186A	Binary-Decimal	3 decades	1 mv to 1.0 v	1	500–5000	1465
192B	Binary-Decimal	4 decades	1 mv to 0.8 v	1	500–5000	1925
202	Binary-Decimal	6 or 10 decades (the 4 decades of the electronic timer can be added to the 6 decades of the scaler)	1 mv to 2.0 v	1	500–5000	2475
8250	Beam-switching	6 decades	0.02 to 5 v negative 5 to 100 v positive	1	none	1760

marized in Table II. The scaler read-outs are in most cases by means of neon glow lamps within the scaling stages, and by digital register for counts exceeding the highest scaling factor. In the case of the Model 8250 scaler (see Figure 38), which is a member of the new "Logic" series of instruments, the read-out is by the so-called *in-line numerical presentation*. This form of read-out is illustrated on the instrumentation shown in Figures 38, 40, and 41. Each of the decade scaling tubes is a "Nixie" tube (trademark of Burroughs Corp.), which is a type of glow-transfer tube (see earlier discussion of this type of component) in which the various positions and configurations of the gaseous discharge are so shaped as to form sequentially the series of numerals from zero through nine.

Sample Handling Systems. Among the complete counting systems offered by

(*Continued on page A468*)

DOUBLE BEAM X-RAY DIFFRACTOMETER

Automatically Records Diffraction Patterns

This instrument incorporates these and many other important features:

- Six scanning speeds, continuous from −90° to +160° of 2θ
- Interchangeable specimen holders (powder, block, integrating)
- Detector position reading from glass circle to 0.01°
- Oscillatory scanning of arcs from 2.5° to 125° of 2θ
- Geiger or scintillation counters with pulse-height analyser

HILGER & WATTS

This diffractometer permits a degree of sensitivity and stability not previously available . . . . . For complete description ask for Catalog CH 322/7.

ENGIS EQUIPMENT COMPANY

431 SOUTH DEARBORN STREET CHICAGO 5, ILLINOIS

AFFILIATED WITH HILGER & WATTS, INC.

A DEMAND FOR MORE . . .

SO NOW THERE ARE FOUR

FOUR BANTAMWARE KITS

The best miniature glassware—Bantamware. The best way to use it—in a Bantamware Kit. And now there are four different kits, for the **exact** set-up you need.

Kit No. 1 has ball and socket type joints on all inclined condenser connections. A second kit is the same, except that it has Teflon® instead of glass stopcock plugs on all appropriate items. A third kit resembles Kit No. 1 but substitutes standard taper joints for ball and socket joints. The fourth kit has tapered joints and Teflon stopcock plugs.

There are over 40 glassware items in each kit—all you need for fractionation, steam, atmospheric and vacuum distillation, chromatographic analysis, extraction, filtration, reflux and separation.

Convenience and utility are provided in all Bantamware Kits. Select one of them for the exact components you need for **your** laboratory.

K-27010 The Original with Ball and Socket Joints $448.00
K-27011 The Original—w/Teflon Stopcocks $444.00
K-27012 A New Kit—Tapered Joints throughout $438.75
K-27013 The New Kit—w/Teflon Stopcocks $442.75

New 32 page Bantamware catalog BW-2 now available. Write for your free copy today.

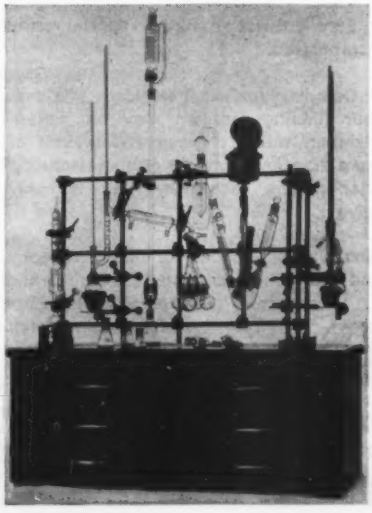
® E. I. Du Pont de Nemours & Co.

bantam-ware®

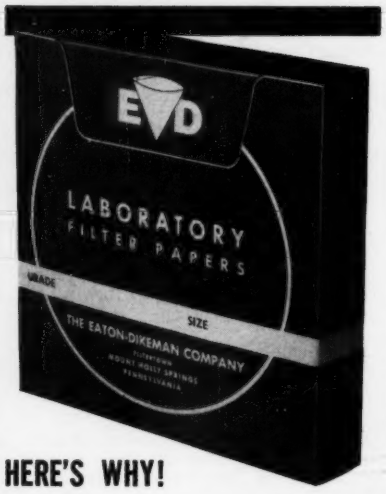
SMALL ORGANIC GLASS APPARATUS

by KONTES GLASS CO.
Vineland, N.J.

"GOOD THINGS IN SMALL PACKAGES"



EATON-DIKEMAN
FILTER PAPER
Used in 7 out of 10 laboratories



HERE'S WHY!

• **Complete range** — whatever rapidity, and retention characteristics you desire, chances are there's a standard E-D paper available. Made with smooth or creped surfaces, in plain or fluted circles, in strips, or rolls, or cut to your individual requirements.

• **Highest purity** — only the purest pulp available is used.

• **Uniform quality** — every step of the manufacturing process is carefully controlled and checked.

• **Excellent wet strength** — special resins incorporated.

• **Complete technical service** — whatever your filtering problem may be, Eaton-Dikeman with its broad background of more than seventy years of manufacturing filter papers exclusively, can probably solve it.

Also available—papers for chromatography and electrophoresis, as well as bibulous and lens papers. Write for free samples.

E D

THE EATON-DIKEMAN CO.
Mount Holly Springs, Pennsylvania

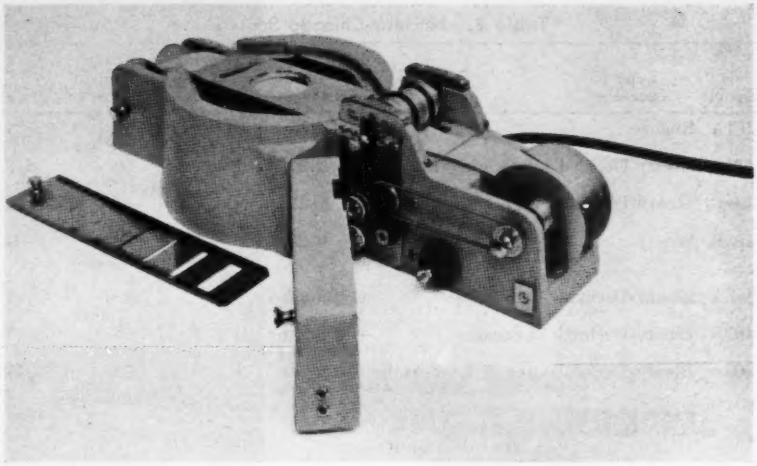


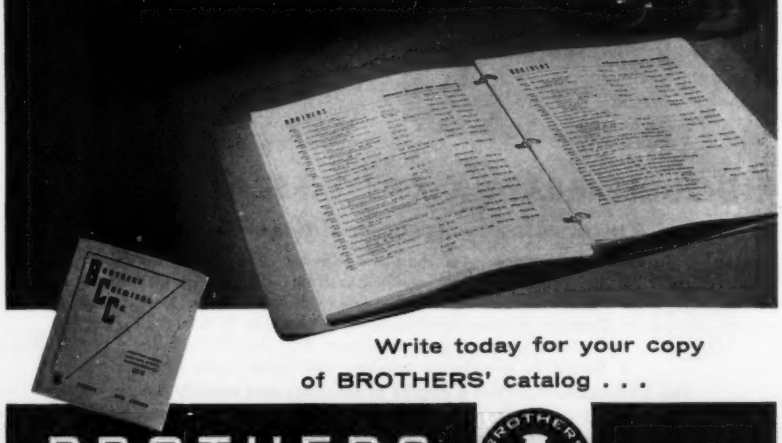
Figure 39. Construction of the paper strip feeder used with the Nuclear-Chicago Model C100A Actigraph II chromatogram scanner. Collimator slit selector is shown at left.

this manufacturer is an automatic low-background system employing a flow gas detector and a cosmic ray guard detector in an anticoincidence circuit, an automatic sample changer holding up to 35 samples, and a printer which makes a record of each sample number and the time required to reach a preselected total count (Model C115 System, without scaler and printer, $4125; Model C111B Printing Timer, $770).

An automatic sample changer for up to 49 gamma-emitting specimens is based upon a scintillation well-detector into which the samples are lowered (Model C120, $2495). A sample handling system for liquid scintillation counting of weak beta emitters, such as C-14 or H-3, includes a temperature-controlled chamber in which the specimen-phosphor preparation can be maintained at any temperature between 0° and 50°F with a constancy of ±1°F, and an automatic sample changing mechanism capable of handling up to 50 specimens (Model 703). For the measurement and delineation of radioactivity distributed on paper chromatograms, a system is available that automatically feeds a paper strip, which may have any

(*Continued on page A470*)

LABORATORY AND REAGENT CHEMICALS



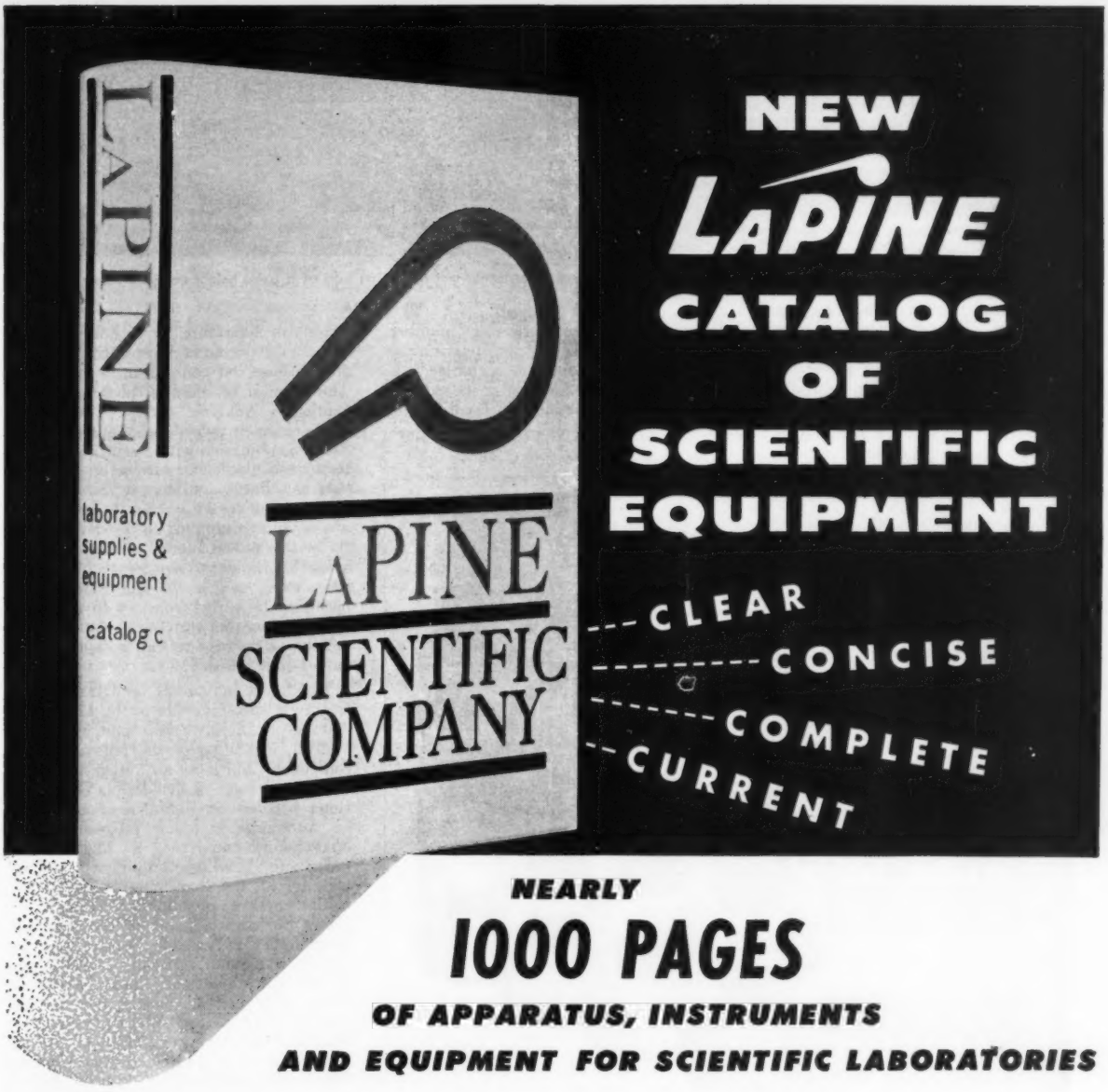
Write today for your copy of BROTHERS' catalog . . .

BROTHERS CHEMICAL CO.
ORANGE, NEW JERSEY

BROTHERS CHEMICAL

Prompt Quotations without obligation.

Serving thousands of laboratories with thousands of reagents.



NEARLY

1000 PAGES

OF APPARATUS, INSTRUMENTS

AND EQUIPMENT FOR SCIENTIFIC LABORATORIES

LaPine Catalog "C" is designed to give scientists and purchasing personnel all the information needed to make correct decisions and purchases.

Catalog "C" is clearly written, fully illustrated. Prices are current with the printing date.

An alphabetical listing and ascending numbering system is used for maximum speed and ease. The comprehensive, extensively cross-referenced subject index pinpoints the location of every item.

SERVICE

LaPine Scientific Company stocks most items listed for immediate shipment from the centrally located Chicago warehouse, or, if the order originates in the east, from the New York warehouse.

CATALOG "C" DISTRIBUTION

Catalog "C" is now being mailed to laboratories and purchasing personnel all across the nation and throughout the world. Please let us know the catalog requirements of your laboratory or department.

LAPINE

LAPINE SCIENTIFIC COMPANY

6001 SOUTH KNOX AVENUE, CHICAGO 29, ILLINOIS, U.S.A.

MANUFACTURERS • DISTRIBUTORS

LABORATORY SUPPLIES • EQUIPMENT • REAGENT AND INDUSTRIAL CHEMICALS

IN THE EAST: *LAPINE SCIENTIFIC COMPANY (NEW YORK) SOUTH BUCKHOUT STREET, IRVINGTON-ON-HUDSON, NEW YORK*

width from $^1/_2$-in. to $1^1/_2$-in., and may be up to 50 ft in length, past a windowless gas flow, or end-window tube detector, while the time axis of a strip chart recorder is caused to run at a synchronous rate. Figure 39 shows the design of the paper strip feed unit (Model C100B Actigraph II Strip Feeder, $545). The feed (and recorder chart) rate may be selected from ten speeds ranging from $^3/_4$ inches per hour to 12 inches per minute. A collimator strip provides a choice of slit openings from $^1/_{16}$-in. to $^1/_2$-in., permitting the operator to select the slit that will give the best compromise between sensitivity and resolution for the radiochromatogram being scanned. This strip feeder requires a detector, ratemeter, and recorder to complete the system (cost of a complete system, about $2100 to $2600, depending upon the type of detector chosen).

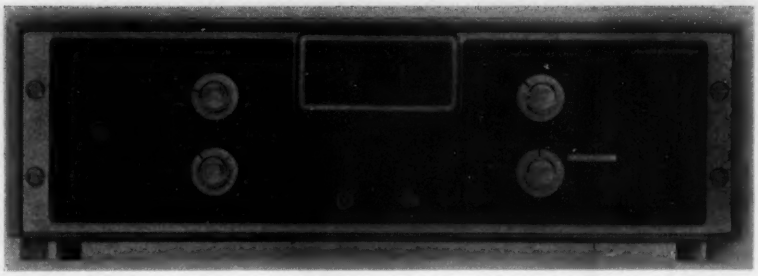


Figure 40. Stepping programmer unit for use as part of a pulse height analyzer in a scintillation spectrometer system.

Gamma Ray Spectrometers. A number of instruments is available for determining the energy spectrum of a radioactive specimen, or for making use of its spectral properties to discriminate in favor of one isotope in a mixture, or to minimize the effects of scattered and degraded radiation on the observed count from a specimen. The simplest of these is the Model 1810 Radiation Analyzer ($885). This is a single-channel pulse-height analyzer for use in combination with a scintillation detector and a scaler or ratemeter. It consists of a linear amplifier, a voltage-regulating circuit for improving the constancy of the voltage supplied to the detector by the scaler or ratemeter, and upper and lower discriminator circuits to provide a *base* level, and a *window width*. The base may be varied from 5 v to 100 v by means of a ten-turn variable potentiometer. The window can be set at any value between 0 and 10 v.

The most advanced of this manufacturer's spectrometers is the Logic 804 Automatic Digital Spectrometry System ($9816), consisting of the following nine component units in an integrated, but modular, design: a five-decade electronic timer, a six-decade digital read-out scaler, an automatic stepping programmer, a dual-channel analyzer, a high-voltage power supply, a linear amplifier, a cooling base for all the electronics, a digital recorder, and a preamplifier. Figure 40 shows the control panel of the stepping programmer (available separately as Model 8551, $960). It makes a maximum of 101 steps per scan, and the digital Nixie tube read-out on the face of the chassis shows the number of the step being read out at any time. The maximum range of the scan is 100 v (in discriminator base level), and each step can be chosen to be 1, 2, 5, or 10 v (window width). The start of the scan can be set at a selection of voltages between 0 and 90 v; the upper limit can be set between 10 and 100 v. When used with a dual-channel analyzer, this unit can be programmed to connect the outputs from the two channels alternately to the scaling and recording units. The electronic timer unit is shown in Figure 41 (available separately as Model 8600, $1695). It contains a crystal oscillator, the frequency of which is electronically scaled down to give output pulses at the rates of 1000 per second for the 0.001 units decimal place, 100 per second for the 0.01 units place, etc. The accuracy of timing is 30 parts per million; drift is 1 part per million per week. The position of the decimal point may be altered by means of a selector switch, so that the range of the timer can be chosen to be 0 to 100 seconds in increments of 1 millisecond, or other ranges up to a maximum of 0 to 100,000 sec in 1-sec increments.

Gives reproducible results, bottle after bottle

Take one set of results you got with Du Pont Sulfuric Acid Reagent. You can change bottles, shipments or locality, and you'll reproduce the same results—time after time! That's because Du Pont continuously runs this reagent through 113 separate analytical tests to keep it uniform for your most stringent requirements.

It's of uniformly high purity, too, exceeding American Chemical Society requirements. And you get the convenience of single-trip cartons, dripless sleeves, safety grips on 5-pint bottles and color-coded caps and labels.

Du Pont's family of reagents includes Nitric, Sulfuric, Hydrochloric and Glacial Acetic acids, and Ammonium Hydroxide. They're readily available all over the country. Ask your local laboratory supply house or write for list of suppliers. Industrial and Biochemicals Department, N-2545 JE, Wilmington 98, Delaware.

BETTER THINGS FOR BETTER LIVING ... *THROUGH CHEMISTRY*

DUPONT
REG. U.S. PAT. OFF.

Other Instrumentation. The preceding paragraphs illustrate the range and versatility of the Nuclear-Chicago line of nuclear instrumentation. It should also be mentioned that this company produces a number of nuclear training aids specifically designed for college and university course work in nuclear physics and chemistry. These range from a demonstration cloud chamber (Model 1413 Cloudmaster, $99) to a Subcritical Training Reactor (Model 9000, $14,950). The Model 4001 Nuclear Training System ($965) is a packaged radioisotope laboratory, including a scaler, timer, G.M. tube, sample mount, four solid radiation sources, five long-lived radioisotope solutions, a choice of several short-lived isotopes, sample preparation materials, and a laboratory manual.

Victoreen Instrument Co.

A complete line of nuclear radiation electronic instrumentation, as well as detectors and special sources, is manufactured by the Victoreen Instrument Company, Cleveland 3, Ohio. Some idea of the range of this company's line may be gained from the selection of instruments listed in Table 3.

An interesting example of Victoreen electronic gear that is useful by itself, and can also be combined with other units to produce specialized systems, is the Model ET-1 Flight-of-Time Detector, ($495) the block diagram of which is shown in Figure 42. This unit functions either as a preset time interval generator, as a gating timer, or as a preset count scaler.

When used as a timer, an internal 60 cps signal (position *A* in the Figure) is fed to the Schmitt trigger circuit, which reshapes the pulses and delivers them to the scale-of-36 circuit, which consists of two glow-transfer tubes. After division by this factor of 36, the signal is a 100 pulse-per-minute frequency. This goes to the 5-decade scaler (scale-of-10^5), consisting of 5 glow-transfer tubes. When the accumulated count on these decades reaches whatever preset value has been selected, the control circuit is activated, and a signal or control pulse is available to turn some other instrument on or off.

When this instrument is used as a gated timer, the gate pulses are supplied to the "gate input" jack. During the period when the gate input is at −10 v, the 60 cps pulses are blocked from passing into the scaling circuits, and the timing indication is suspended. Thus, the form of the gate signal will determine the periods during which the timer is "alive" and "dead," respectively.

To use this instrument as a preset scaler, the input selector switch is set to the scaler input (position *B* in the Figure). The impulses from the scaler then pass through the Schmitt trigger (which now functions as a pulse height discriminator in addition to a pulse shaper) and enter the scaling decades. When any preselected number of counts has been reached, the control circuit is activated, and the output or control signals are generated.

Figure 43 shows a block diagram of the most sophisticated and recent of Victoreen instruments, viz., a transistorized 200-channel spectrometer. This instrument has two independent input circuits, and can accept simultaneous signals from, e.g., two scintillation detectors. In the analog-to-digital converter, each pulse (of any amplitude from zero to the maximum produced by the sample) is converted into one of the numbers from 0 to 199. Clock pulses at 2.0 megacycles per second are "gated" by the pulse being converted; i.e., if the pulse has a duration of 2 microseconds, then 2 millionths of the 2-megacycle/sec clock pulse, or a total of 4 pulses, are allowed to pass. These digital signals are fed into the "address scaler," which sorts them, i.e.,

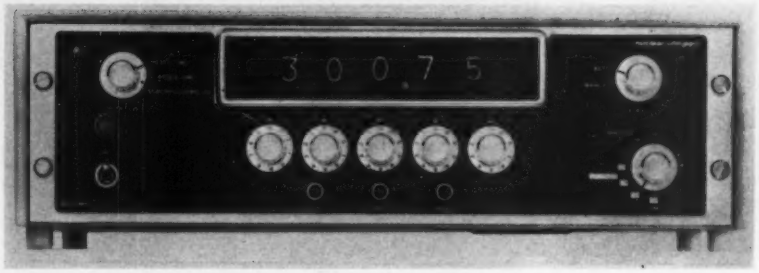


Figure 41. Model 8600 electronic timer unit of Nuclear-Chicago.

(*Continued on page A474*)

NOW the accuracy of glass in breakproof Nalgene graduates

New Nalgene graduated cylinders feature calibration to best glass standards, in accordance with federal specifications.

New Nalge techniques give you accuracy never before possible in plastic, or even in glass, because now for the first time graduates can be *molded* to absolute uniformity *every time.* You get finer calibration lines than ever before. Meniscus is flat, easy to read. Non-wetting walls contain and deliver the same amount of solution every time.

Corrosion resistant, of course. Virgin polypropylene throughout, with stable octagonal base. No more loss of valuable contents and no dangerous acid splash through breakage. So next time you break a glass graduate, replace it with Nalgene—complete line of sizes from 25 to 2000 ml. Ask your laboratory supply dealer.

Nalge makes them unbreakable ... and keeps making them better!

Accuracy tested, accuracy proved!

A random sampling by a nationally-known testing laboratory* shows new Nalgene graduates to be well within National Bureau of Standards Class A specifications for accuracy. Actual calibrations found in tests on 50 ml graduates:

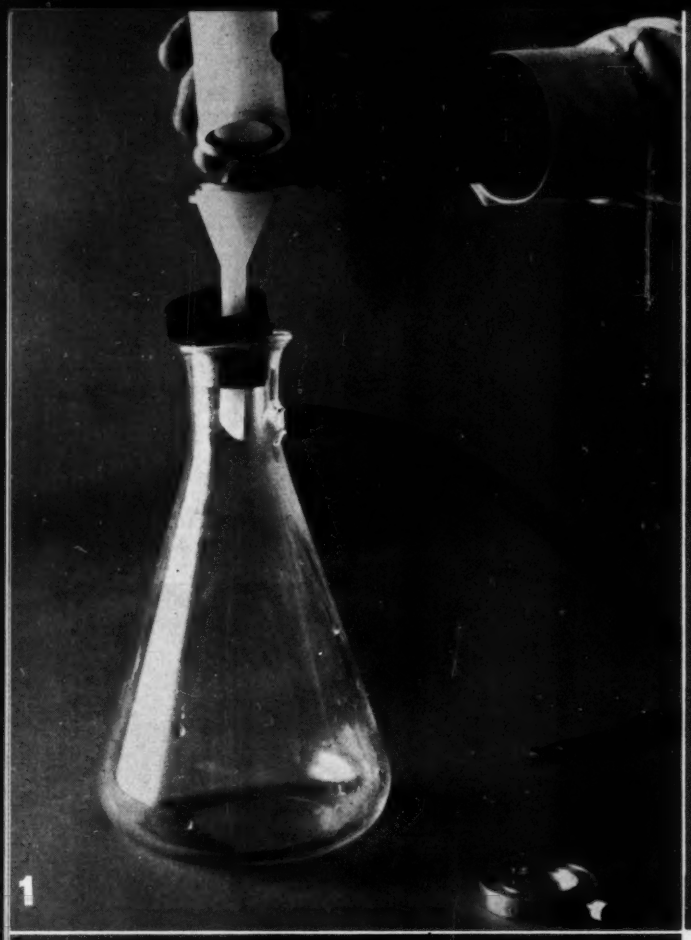
Capacity, ml.	10.00	20.00	30.00	40.00	50.00
Nalgene Instrument No. 12	10.01	19.99	29.86	39.92	50.01
Nalgene Instrument No. 13	10.04	19.99	29.87	39.88	49.92
Nalgene Instrument No. 14	10.07	20.03	29.89	39.87	49.97

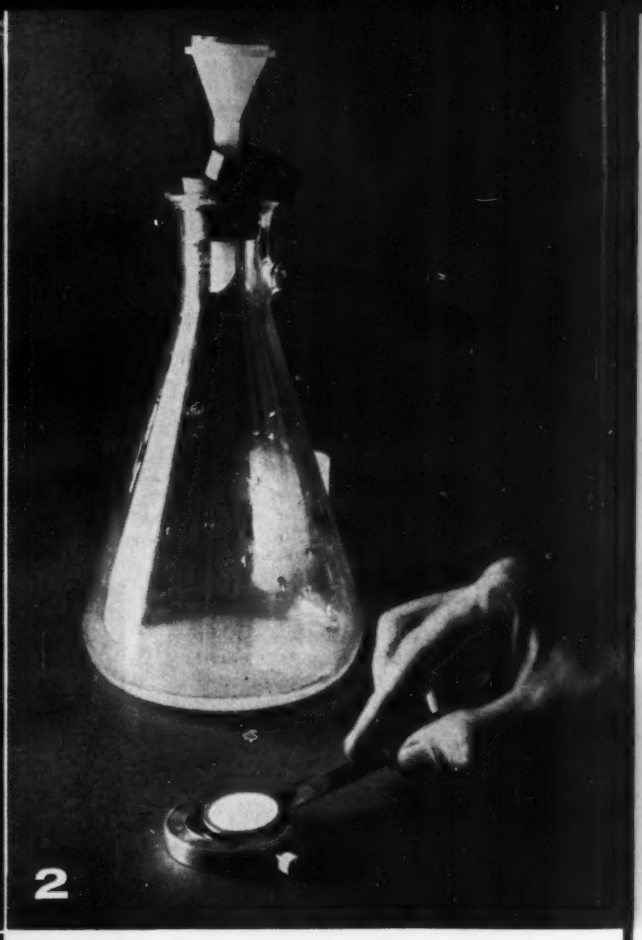
*Name and data on request.

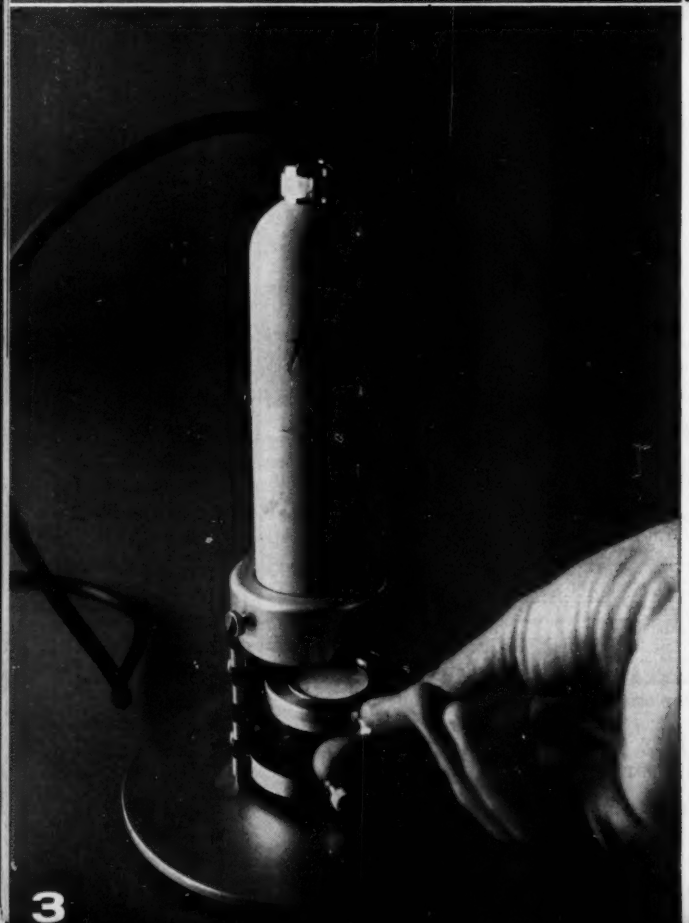
New complete line catalog. WRITE Dept. 187.

THE NALGE CO., INC.
ROCHESTER 2, NEW YORK

The Quality Standard of Plastic Laboratory Ware







Students Prepare Radioactive Precipitate in Minutes

The single most outstanding feature of the new 4001 Nuclear Training System is ease of sample preparation. Nuclear-Chicago has developed a simple and unique chimney funnel which contains a porous steel disc on which the radioactive precipitate is deposited. The technique is simple and consists of three easy steps: (1) The porous sample disc is placed in lower portion of the funnel. Chimney holds disc in place. (2) Suspension of radioactive material is added and liquid phase filtered off. Disc with radioactive deposit is removed, dried, and placed in sample-pan holder. (3) The holder is inserted into three-level sample mount for counting. The disc is easily cleaned and may be used repeatedly. Entire procedure takes only minutes.

Model 4001 Nuclear Training System

Shipped complete with Scaler, Timer, Mount, Geiger Tube, Radionuclide Set, two Sample Preparation Sets, Solid Source Set, Radionuclide Certificate Book, nine Experiment Manuals, and Instructor Notes Manual. The Model 4001 system provides all the radioactive reagents, instruments and accessories required by the experiments. **Price $965.00**

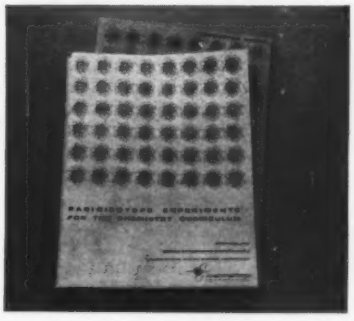
Nuclear-Chicago offers complete classroom nuclear laboratory, 33 special radiochemistry experiments

Student experiments, platform demonstrations, postgraduate research. Radioisotope training can now be incorporated into every chemistry class with the first complete low-cost nuclear laboratory developed for schools. Model 4001 system is a precise teaching aid supplied with specially prepared course material to integrate radiochemistry into the course curriculum without disrupting existing experiments. Though its precision and reliability make it valuable in radiochemical research, operation is so simple that it may also be used in advanced high-school teaching.

New insights and new interests come from the dramatic use of radioisotope procedures in conventional classroom experiments. While the important chemical subject matter is taught, the instructor can at the same time include nuclear techniques as a secondary feature *. . . without having to change course material.* With the 4001 system, radioactivity is presented naturally as another tool with which to solve the practical problems of science.

The fact that students may have had little or no experience in handling radioisotopes is recognized in the practical experiments contained in the laboratory manuals supplied with the 4001. Even spills present no serious problem because of the extremely low amount of radioactivity used by each student. No license from the Atomic Energy Commission is required to purchase or use the isotopes supplied with the system. Most of the experiments presented in the manual are planned so that one generally licensed package of radioactive chemical will suffice for 30 or more students.

33 radioisotope experiments for the chemistry curriculum. Full emphasis on the chemical principles rather than the technical aspects of radioisotopes is given in the 33 specially developed experiments. The 187-page Laboratory Manual and the 60-page Instructor Notes Manual provide a detailed, comprehensive source of radioisotope information and experiments. Fifteen of the experiments illustrate the properties of radioisotopes and the instruments involved in their detection and measurement. The remaining 18 emphasize the role of radioactivity in chemical analysis.



Send for free text. A copy of the 187-page Laboratory Manual and further information on the 4001 system are available to educators at no charge. Please request your copy of the Chemistry Experiment Manual and 4001 brochure.

nuclear-chicago
CORPORATION

343 East Howard Avenue, Des Plaines, Illinois

Table 3. Selected Victoreen Nuclear Instruments.

Type	Remarks	Model	Price
G.M. Survey Meter, Beta-Gamma	Transistorized power supply; uses one 1.3-v and one 4.5-v battery	389C	$ 250
Scintillation Detector Survey Meter, with Probe	Same as above	645, with 587B Probe	495
Cutie-Pie Survey Meter	0.00025 in. Mylar window; uses four 22.5-v and one 1.3-v batteries; ±10% accuracy. 0–100 to 0–10,000 mr/hr ranges	740	275
Linear Count-Rate Meter	10 ranges; 0.5% minimum probable error	CRM-2	370
Scaler, Decimal, 3 Decades, 2500-v HV Supply	Resolving time 5 microseconds; input sensitivity -5 v	S3HV25	655
Scaler, Decimal, 2 Decades, Glow-transfer Tubes	Resolving time 200 microsec; input sensitivity 0.25 to 5.0 v; contains 500–2000 v HV supply	S2-GT	390
Scaler, Decimal, 3 Decades, with Regulated HV Power Supply	Resolving time 2 microsec; input sensitivity 50 v; power supply in separate chassis	Univic 764-1 and 765-1 HV Supply	1035
Single-Channel Pulse-Height Analyzer	Range 0-85 v; window 0-8.5 v; for use with a linear amplifier and a scaler or ratemeter	PHA-2	555
Precision Automatic Single-Channel Spectrometer, with Printer and Recorder	100-step scan; gives both a digital and an analog read-out	ASP-1ADR	5450

determines which of the 200 channels each signal belongs in, and sends a pulse to the appropriate place in the core memory. This memory circuit consists of a number of ferrite discs, each of which may be in one of two states of magnetization, viz., each is either in an "on" or "off" (or, "yes" or "no") state. Thus, by connecting up the ferrite disks in suitable combinations, and employing the logic and algebra of the binary number system, the total number of pulses fed to a given location on the memory core can be read out at any subsequent time by determining the states of magnetization of the various ferrite discs. This stored digital information is read out directly on the printer, and is also converted back to an analog form for presentation on the face of an oscilloscope (CRT = cathode ray tube) screen, and for application to a strip-chart recorder. The spectrometer circuitry is designed so that the input signals in the two channels may be added or subtracted, as desired, or the two channels may be read out separately. The print-out speed is 4 channels per second.

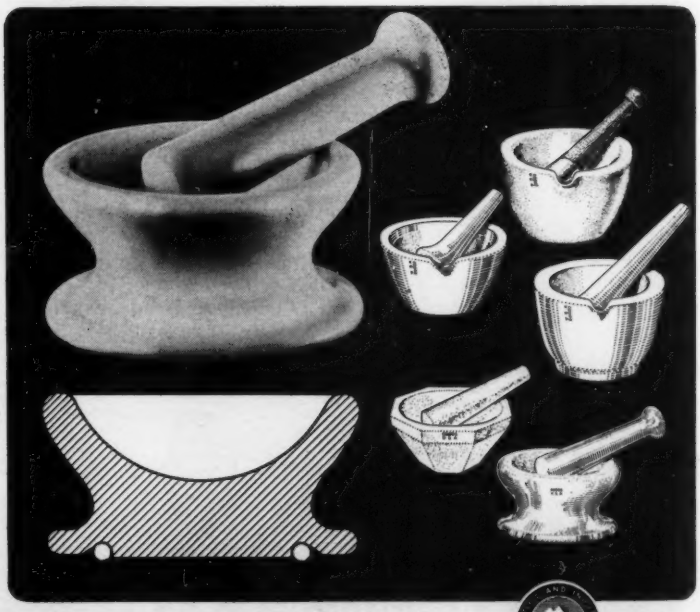
Gamma ray spectrometers are gaining rapidly in popularity, largely because of the fact that scintillation detection is capable of greater sensitivity, reproducibility, and specificity than any of the other detection techniques. The spectrometer permits the maximum use to be made of the information potentially present in the output of the scintillation detector. Also, scintillation detectors can be combined in various ways, e.g., in parallel as shown in Figure 44, which are not practical for electrical pulse detectors (as distinguished from these, which are optical pulse sensors).

Radiation Instrument Development Laboratory

A complete line of detectors, sources, and electronic gear for radiation measurement is also available from Radiation Instrument Development Laboratory, Northlake, Illinois. This manufacturer has specialized principally in the production of electronic gear for laboratory measurements, as distinguished from, e.g., survey meters and personnel dosimeters. The instruments currently in production include representatives of the types of power supplies, amplifiers, rate-

(*Continued on page A476*)

COORS U.S.A. Mortars & Pestles



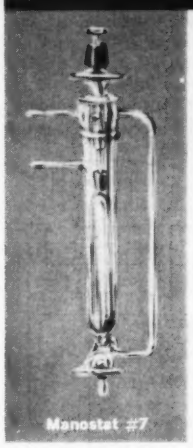
Coors offers a wide variety of mortars and pestles—shapes, sizes and materials. Of particular importance is the Coors Alumina Mortar and Pestle, designed by Coors to meet the requests of chemists and technicians. Made of 96% aluminum oxide, it has extremely high mechanical strength. Sapphire hard, it resists surface wear and consequent sample contamination. Polished grinding surfaces stay smooth, easy to clean. Unique shape of mortar is easier, more comfortable to hold. The exclusive rubber ring included in the base (patent pending) prevents slippage and accidental loss of sample.

Available through your local laboratory supply dealer

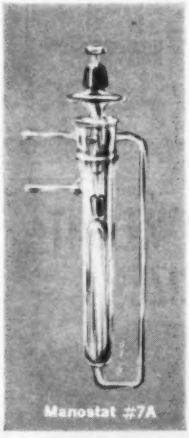
COORS PORCELAIN COMPANY GOLDEN, COLORADO

precisely engineered, performance-proved laboratory instruments for

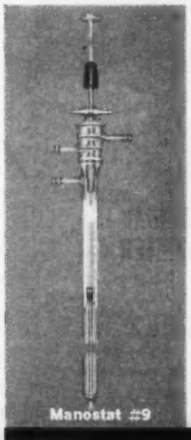
AUTOMATIC PRESSURE, VACUUM AND FLOW CONTROL


Manostat #7

Automatic vacuum and pressure control with remarkable vacuum memory feature. Almost uncanny in its human-like sensitivity and accuracy of performance! Literally memorizes the last setting, so that a system which is shut down returns to precisely the same setting when operation is resumed. This all-glass instrument is ideally suited to laboratory applications because of its corrosion resistance. Can be used to control vacuum, pressure or flow. Sensitivity: ± 0.2%, capacity: 8 liters/min. #7, all-glass model, ready for use, with rubber connections. Mercury not included .....ea. **$54.00**

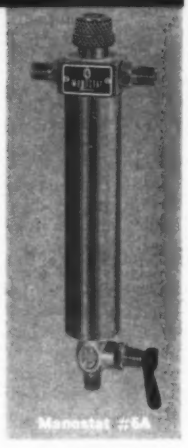

Manostat #7A

Identical in construction and performance to #7, but without the 3-way stopcock at the base. For pressure and vacuum control, this easy-to-operate instrument, with the vacuum memory feature is the most economical Cartesian Manostat available. Sensitivity: ± 0.2%, capacity: 8 liters/min. #7A, all-glass model, ready for use, with rubber connections. Mercury not included .....ea. **$46.00**


Manostat #9

Construction essentially similar to #7A, but with the addition of a 100 mm. scale which permits use of the instrument not only for controlling pressure, absolute or differential, but for measuring it as well. Sensitivity: ± .05 mm. to 0.2 mm., capacity: 8 liters/min. #9, complete, ready for use, with 2 floats: 0-10 mm. in 1/10 mm. divisions and 0-100 mm. in 1 mm. divisions. Mercury not included.

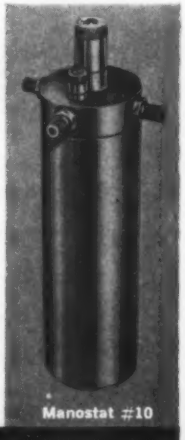
ea. **$104.00**


Manostat #6A

Automatic vacuum, pressure and flow control with vacuum memory feature, convenient toggle valve operation, and interchangeable orifices. The most versatile of all Manostats! Sensitivity: ± 0.2%, capacity: 32 liters/min. #6A, all stainless steel, with 1 mm. orifice. Mercury not included .....ea. **$140.00**

Manostat #8

Automatic vacuum and pressure control, with amazingly simplified operation. Place this self-contained unit in your system, set it – forget it! Corrosion-resistant anodized aluminum body, with needle valve by-pass (to replace stopcock). Exceptionally high sensitivity: ± .05%, and high capacity: 130 liters/min. #8, complete with 3 interchangeable orifices. Mercury not included .....ea. **$155.00**


Manostat #10

The ultimate in design and performance. Absolute, simplified one-element control of vacuum, pressure and flow. Incorporates the outstanding memory feature which remembers your vacuum setting even after system is shut down. Offers the significant advantages of fine control for highly critical applications, plus increased capacity. Can be employed anywhere, from research to production. Sensitivity: ± 0.1%, capacity: 500 CFM. #10, complete with mercury and ready for use.

ea. **$350.00**

For complete information on any or all of these Cartesian Manostats, write for specific bulletins.

The EMIL GREINER *Co.*

20-26 N. Moore Street, Dept. 422, New York 13, N. Y.

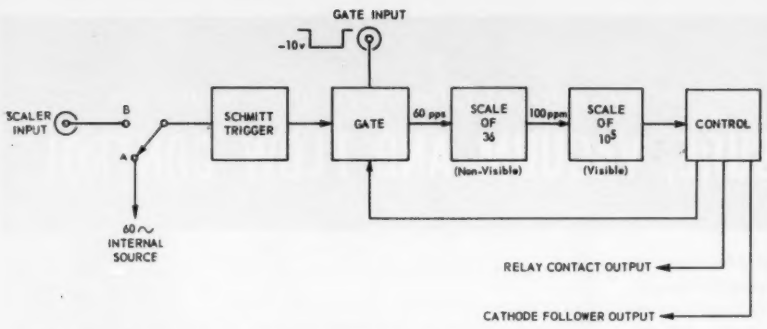


Figure 42. Block diagram of the Victoreen Model ET-1 Flight-of-Time Detector.

meters, scalers, low-level counting systems, pulse height analyzers, and spectrometers already described above in connection with other manufacturer's products.

An interesting feature of several R.I.D.L. scalers is the numerical read-out indicator illustrated in Figure 45. In this case, a conventional decimal scaling stage is employed, and the total number of pulses received determines which of the ten lamps will be lit at any moment. The lamp that is on projects an image of of its associated numeral onto a viewing screen. This gives a larger visual presentation than is commonly used on decimal scalers.

R.I.D.L. has been active in the development of multi-channel analyzers, and has produced models with as many as 2000 channels. Currently, transistorized 200- and 400-channel analyzers are in production. These instruments utilize a magnetic core memory unit, analog-to-digital conversion, cathode ray tube display, and printer read-out.

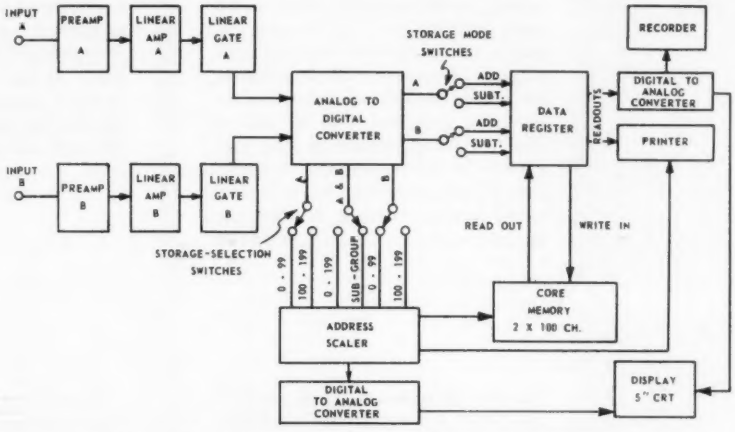
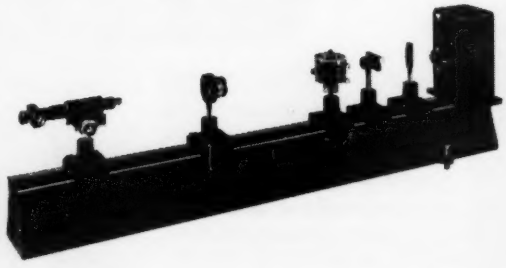


Figure 43. Block diagram of the Victoreen Model ST-200D dual input 200-channel spectrometer.

Radiation Counter Laboratories

A particularly extensive line of nuclear detectors and electronic gear is available from Radiation Counter Laboratories, Skokie, Illinois. This company manufactures a wide variety of G.M., proportional, gas flow, and neutron detectors, as well as specialized glassware and accessories. In addition to a full arsenal of conventional vacuum tube instruments, this manufacturer has introduced a complete line of transistorized instruments

Direct Measurement of Difference in Refractive Index



The New Brice-Phoenix Differential Refractometer uses a split cell to measure the difference in refractive index between a dilute solution and its solvent.

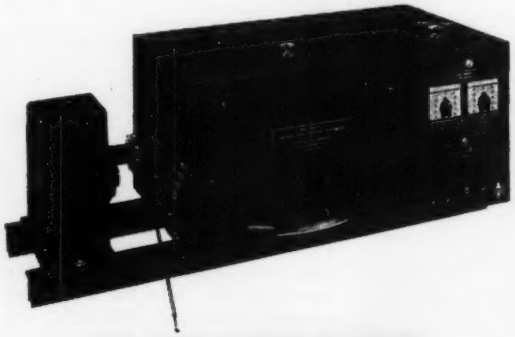
Sensitivity 3 X 10⁻⁶.

For complete details write Dept. CE-3

PHOENIX PRECISION INSTRUMENT COMPANY

3803-05 N. 5th St. Philadelphia 40, Pa.

MEASURE MOLECULAR WEIGHT AND PARTICLE SIZE



NEW BRICE-PHOENIX UNIVERSAL LIGHT SCATTERING PHOTOMETER

Measures:

1. Absolute Turbidity
2. Dissymmetry
3. Depolarization

This instrument is listed in U.S. Government specifications for the evaluation of certain clinical materials.

For complete details write Dept. CE-2

PHOENIX PRECISION INSTRUMENT COMPANY

3803-05 N. 5th St. Philadelphia 40, Pa.

composed of modular building blocks which can be combined in a variety of ways to form different systems. In addition, each module contains its circuitry in the form of plug-in printed circuit boards, which can be quickly and conveniently removed for testing, or replaced for repair or to redesign the module. This type of instrument design is shown in Figure 46.

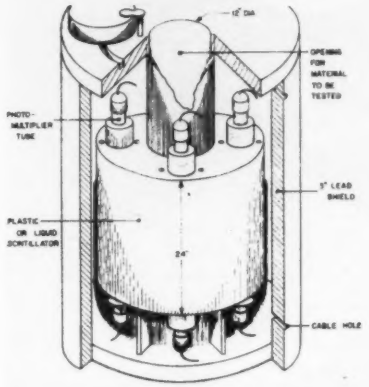


Figure 44. A typical low-level scintillation counter in which a ring of photomultipliers surrounds the scintillator well.

The four-module instrument shown consists of, from right to left in the Figure, a high voltage supply (No. 20703, $615), a linear amplifier with discriminator (No. 20112, $535), a five-decade scaler (No. 20303, $920), and a timer (No. 30904, $643). A low voltage supply (No. 20710, $550) is also required, and is contained in the instrument cabinet at the rear of the modules. The scaler module can be replaced by a ratemeter module if continuous read-out is desired. The linear amplifier module can be substituted by a single-channel pulse-height analyzer if spectral analysis is required; automatic analysis can be obtained by using an electronically swept single-channel analyzer module, and connecting a recorder to the output plug of the ratemeter module.

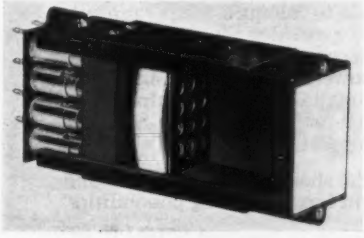


Figure 45. Numerical read-out display unit utilized in some of the instruments of Radiation Instrument Development Laboratory. The numeral that is seen is selected by electronic choice of one of the lamps, which then projects the image of the digit in its path onto the screen.

R.C.L. has been one of the pioneers in the commercial development of gamma ray spectrometers with magnetic memory cores, and its most recent instrument of this type is a 2048 Channel Analyzer with

(Continued on page A479)

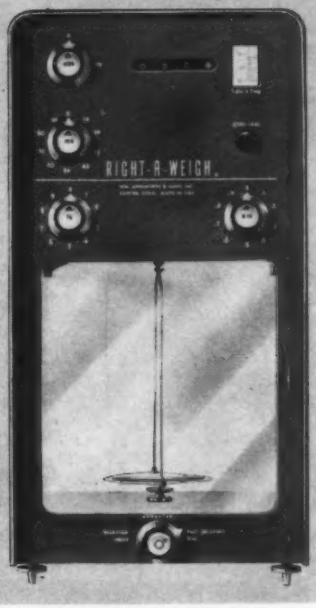
AINSWORTH

Premium Quality at Competitive Price

Made in U.S.A.

RIGHT • A • WEIGH

Substitution Weighing Balance



FAST
ACCURATE
EASY TO USE

CONTROLS

All controls on front of case, clearly designated. Independent pan brake stabilizes the pan before beam is released. Simple mechanical zero adjustment, large range, no distortion. Easy-working doors with comfortable finger-grips.

READOUT

Eye-level, in-line, unobstructed readout. Wide-spaced lines on projected scale. Projection scale in recessed shadow box. Light filter in optical path cuts out glare.

FAST *...weighing procedure is simply to load pan, dial weights, read results.*

ACCURATE *...substitution weighing eliminates arm-length errors, gives constant sensitivity and accurate values.*

EASY TO USE *...anyone can weigh quickly and accurately with the Right-A-Weigh ... frees skilled people for other work.*

Capacity: 200 g. Sensitivity: 1/10 mg. Readability: 1/20 division on projected scale using vernier. Reproducibility: ±0.03 mg.

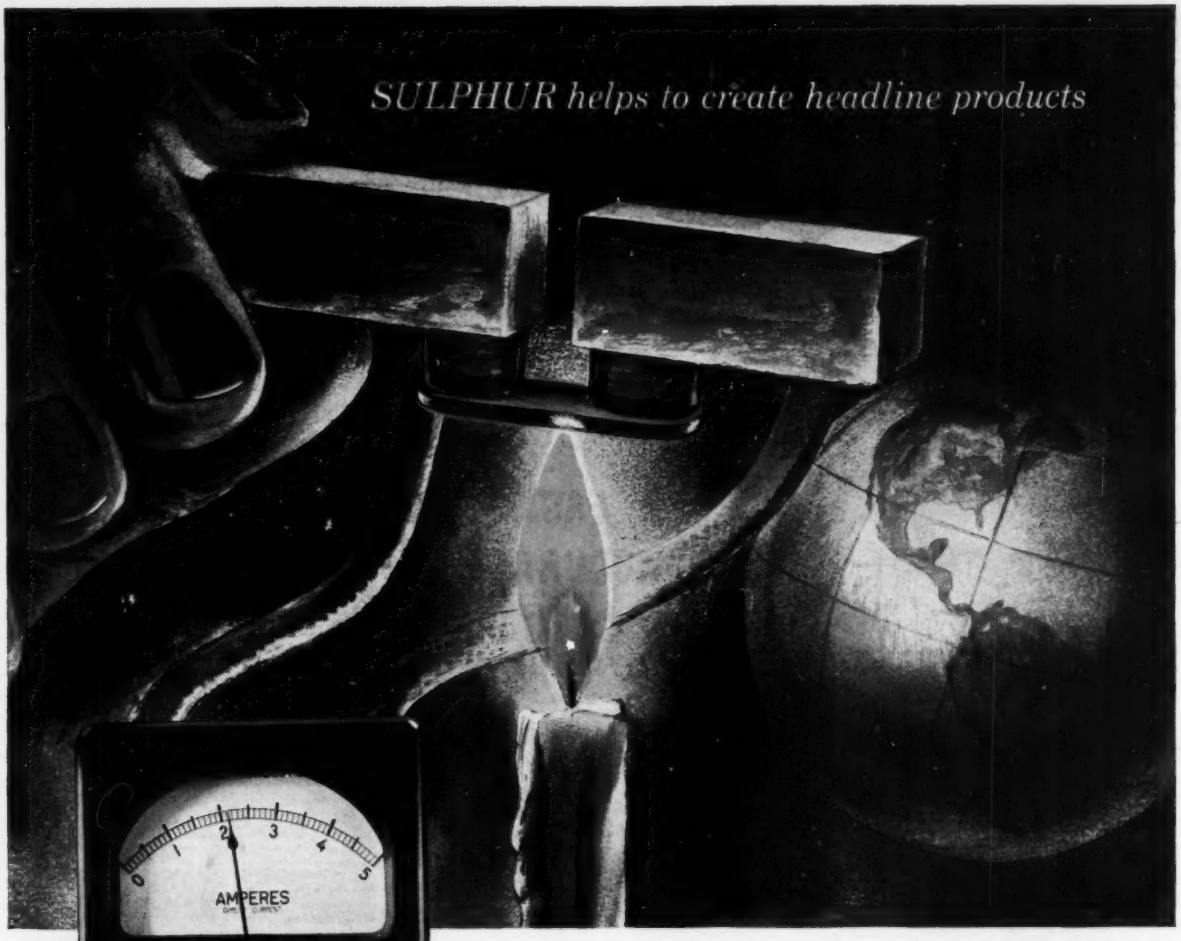
Special Models: SCX, explosion proof; SCD, diamond balance calibrated in carats; SC 300, 300 gr. cap.

AINSWORTH

WRITE FOR BULLETIN 659.

Symbol of Quality & Progress Since 1880.

WM. AINSWORTH & SONS, INC.
2151 LAWRENCE ST. · TELEPHONE ALpine 5-1723 · DENVER 5, COLORADO

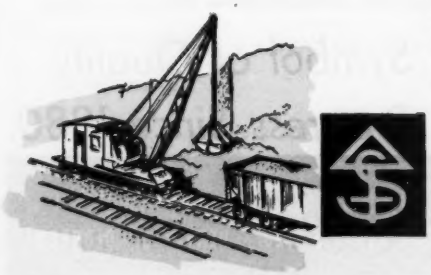


Will sulphur help to light the world?

That would be a large order and maybe the idea is in the land of fantasy but an interesting development involving sulphur has come from the Westinghouse Research Laboratories—electricity from a thermoelectric material heated to a very high temperature. The use of a thermocouple of dissimilar metals to measure temperature is, of course, not new and when so used generates a voltage. Today, through improved materials, the same concept is being developed to generate useful amounts of electric power. Recently, Westinghouse scientists discovered that two man-made rare-earth sulphides—Cerium Sulphide (Ce_2S_3) and Samarium Sulphide (Sm_2S_3)—can produce such power at very high temperatures.

Science has long been searching for the short cut between heat and power. This Westinghouse development has interesting possibilities.

As of the moment no 'tonnage' of sulphur is involved in this Westinghouse development but millions of tons of TGS Sulphur do go into industry annually from our producing properties in the States and Canada. Our regional terminal storage facilities for molten sulphur with short haul deliveries have greatly broadened the TGS service to industry.



TEXAS GULF SULPHUR COMPANY

75 East 45th Street, New York 17, N. Y.

811 Rusk Avenue, Houston 2, Texas

Sulphur Producing Units: Newgulf, Texas • Moss Bluff, Texas • Fannett, Texas Spindletop, Texas • Worland, Wyoming • Okotoks, Alberta, Canada

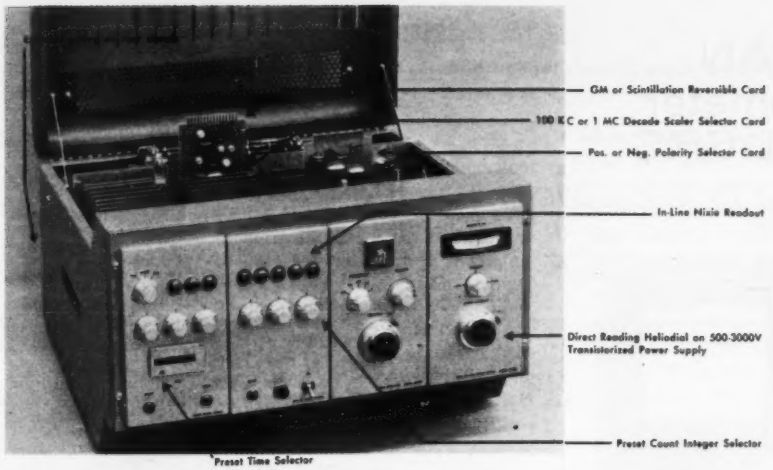

GM or Scintillation Reversible Card
100 K C or 1 MC Decade Scaler Selector Card
Pos. or Neg. Polarity Selector Card
In-Line Nixie Readout
Direct Reading Heliodial on 500-3000V Transistorized Power Supply
Preset Count Integer Selector
Preset Time Selector

Figure 46. Illustrating the design of the Radiation Counter Laboratories line of transistorized nuclear instruments, featuring the use of plug-in circuit boards and modular construction.

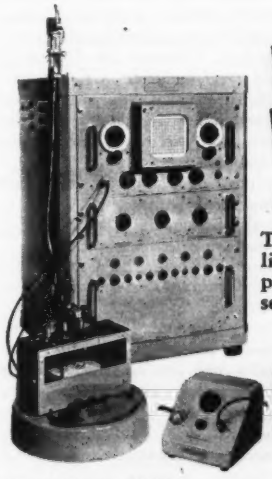
which it is possible to use 16 different inputs of 128 channels each, or any combination of these units.

Other specialized R.C.L. instrumentation includes a slow-neutron time-of-flight analyzer, a 5-decade glow tube scaler kit (No. 20304K, $249), a neutron generator for nuclear activation work, and walk-in, low-level counting systems for whole body monitoring.

Other Manufacturers

The preceding descriptions should suffice to show the great variety of commercial instrumentation currently available in the nuclear field, and the multiplicity of manufacturers. Those companies which have been treated above are, however, only several among many in this field. Space does not permit giving equal treatment to all the instrument makers who are currently producing nuclear measuring equipment. The companies that were selected for detailed description above were those which produce the prinicpal types of instruments either in their most typical

(Continued on page A480)



A COMPLETE POLAROGRAM

Every Seven Seconds...

The entire change of potential is effected during the lifetime of a single mercury drop...and the entire polarogram is reproduced on the screen once every 7 seconds, cutting analysis time to a fraction!

The Cathode Ray

POLAROTRACE

WITH ELECTRODE STAND

Now available with ANODIC CONVERSION UNIT to make possible measurement of anodic waves. Camera attachment also available.

Polarotrace is a product of SOUTHERN ANALYTICAL, LIMITED CAMBERLY, SURREY, ENGLAND

Determines concentrations OVER A THOUSAND TIMES LOWER than conventional types of polarographic instruments.

For DIRECT or Derivative Operation • Faster • More Sensitive Greater Resolution • Easier to Operate • Ruggedly Designed

Cat. No. JC-83725—POLAROTRACE, with Electrode Stand.....$4,500.

DETAILED INFORMATION AVAILABLE UPON REQUEST

Our application laboratory is at your disposal to run test specimens.

STANDARD SCIENTIFIC Supply Corp. 808 BROADWAY NEW YORK 3, N.Y.

LABORATORY APPARATUS REAGENTS AND CHEMICALS

FREE S·S Reference Sheets on Selectacel®

ION EXCHANGE CELLULOSES

for use in chromatographic columns

New Selectacel Ion Exchange Celluloses have remarkable properties when used with ionic and colloidal materials of high molecular weight.

Such applications include—

- ENZYMES
- PROTEINS
- HORMONES
- LIPIDS
- NUCLEIC ACIDS

These materials produce separations that far exceed what usually can be accomplished alone by ion exchange resins, chromatography, electrochromatography, or electrophoresis.

There are several kinds of Selectacel Ion Exchange Celluloses:

ANION EXCHANGERS

Type	Grade	Capacity meq/g
DEAE (Diethylaminoethyl Cellulose)	Standard	0.9
	20	
	40	

Separation and purification of proteins, peptides, enzymes, hormones and related materials.

Type	Grade	Capacity meq/g
ECTEOLA (Epichlorohydrin triethanolamine)	Standard	0.3
	20	
	40	

Separation and purification of viruses.

CATION EXCHANGERS

Type	Grade	Capacity meq/g
CM (Carboxymethyl Cellulose)	Standard	0.7
	20	
	40	

Weakly acidic—most effective at pH's slightly above 4.

Type	Grade	Capacity meq/g
P (Cellulose Phosphate)	Standard	0.9

Bifunctional—containing both strongly acidic and weakly acidic groups. Relatively high exchange capacities.

MAIL COUPON TODAY

Send for these new free Selectacel Reference Sheets today—no obligation of course.

S·S

Carl Schleicher & Schuell Co.
Keene, New Hampshire
Department JC-7

Send FREE Selectacel Reference Sheets.

NAME_____

COMPANY_____

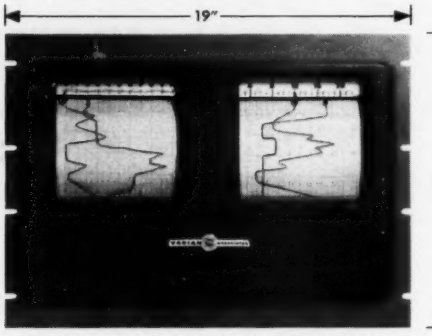
ADDRESS_____

CITY_____ STATE_____

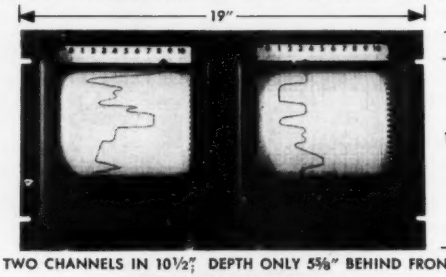
Selectacel is manufactured by Brown Company and exclusively packaged and distributed for laboratory use by S & S.

VARIAN
Potentiometer
RECORDERS

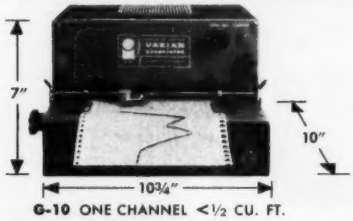
More performance in less space



G-22 FOUR CHANNELS IN 14"; DEPTH ONLY 11½" BEHIND FRONT PANEL



G-11A TWO CHANNELS IN 10½"; DEPTH ONLY 5⅜" BEHIND FRONT PANEL



G-10 ONE CHANNEL <½ CU. FT.

THREE COMPACT CHOICES

Using one quarter the space of many comparable potentiometer recorders, the Varian family packs exceptional function into very little space. Interchangeable input chassis accommodate full-scale signal voltages from 10mv to 500v d.c., temperatures from −200°C to +1500°C, and 1mA current recording. The Varian recorders have 1% accuracy, ¼%-of-span sensitivity, 1 or 2½ second balancing time, full-span zero adjust, Zener diode or mercury cell reference. A selection of chart speeds from ⅛"/hour to 16"/minute lets you pick the time resolution you need.

In addition to being rack-mountable, the G-22 and G-11A are portable for use in many locations. A wide range of accessories—such as retransmitting slidewires, alarm contacts and event markers—helps broaden the outstanding functional versatility outlined above. Chances are a Varian recorder can serve your need. Write Instrument Division for detailed specifications.

VARIAN associates
PALO ALTO 54, CALIFORNIA

NMR & EPR SPECTROMETERS, MAGNETS, FLUXMETERS, GRAPHIC RECORDERS, MAGNETOMETERS, MICROWAVE TUBES, MICROWAVE SYSTEM COMPONENTS, HIGH VACUUM EQUIPMENT, LINEAR ACCELERATORS, RESEARCH AND DEVELOPMENT SERVICES

form or in a form most amenable to this type of descriptive explanation. Since the principal types of commercial instruments have now already been treated, in the form of specific examples, we shall now only list the remaining major producers and distributors of these types of instruments.

Ad-Yu Electronics Lab., Inc., Passaic, New Jersey—*delay lines.*

Ameray Corp., Kenvil, New Jersey—*shielding.*

American Tradair Corp., Long Island City 6, New York—*importer of EKCO Electronics, Ltd., England, scalers, scintillation counting systems, detectors, general electronics.*

Applied Physics Corp., Cary Instruments Div., Monrovia, California—*ionization chambers and electrometer amplifiers.*

Atomasters-Buntaine Corp., St. Louis 22, Missouri—*distributor of sample preparation and handling equipment, and electronic gear.*

Atomic Accessories, Inc., Valley Stream, New York—*distributors of complete line of nuclear supplies and instrumentation, including training aids and kits.*

Atomic Center for Instruments and Equipment, New York 17, N. Y.—*distributor of survey meters, scalers, other equipment.*

Atomic Products Corp., Center Moriches, Long Island, New York—*accessories and handling equipment.*

Atomium Corp., Waltham 54, Massachusetts—*specialized detectors and counting systems.*

Automation Inc., Los Angeles 44, California—*precision scaler.*

Baird-Atomic, Inc., Cambridge 38, Massachusetts—*complete line of electronic gear and counting systems.*

Beckman Instruments, Berkeley Division, Richmond California—*electronic timing, counting, and digital printing equipment.*

Detectolab, Inc., Chicago 26, Illinois—*probes and precision electronic gear, including spectrometers.*

Eldorado Electronics, Berkeley 10, California—*precision electronic gear, from scalers to spectrometers.*

Forro Scientific Co., Evanston, Illinois—*radiochromatogram scanner.*

General Electric, Schenectady, New York—*detectors, and some electronic units.*

Gyra Electronics Corp., La Grange, Illinois—*power supplies, electrometer amplifiers, ratemeter.*

Hamner Electronics Co., Inc., Princeton, New Jersey—*precision electronic gear from power supplies to automatic gamma spectrometers; also some detectors, esp. neutron counters.*

Hewlett-Packard Co., Palo Alto, California—*electronic counters, timers and digital printers.*

Hughes Aircraft Co., Nuclear Electronics Lab., Los Angeles 45, California—*solid state radiation detectors.*

Hupp Instrumentation, Los Angeles 25, California—*electronic timers and counters.*

International Nuclear Corp., Nashville 11, Tennessee—*scalers, pulse height analyzer.*

Interstate Electronics Corp., Anaheim, California—*coincidence analyzer.*

Isotopes, Inc., Westwood, New Jersey—*phosphors, beta flow counter.*

(Continued on page A482)

Kodak reports on:

the competitive assault on salt . . . anthracene: decent, pure, purest, hyper-pure . . . the relativity of rapidity

Cellmakers

Charles W. Warren

Paul A. Wilks, Jr.

Meet the founders of Connecticut Instrument Corporation, Wilton, Conn., POrter 2-5545. You can call them up and order any of a number of infrared accessories, including one they call a "C.I.C. Irtran-2 Fixed Thickness Absorption Cell" for $160. This fits directly into the standard cell slides of two of the more popular infrared spectrophotometers. Transmittance: better than 60% from 2 to 12μ. Clear aperture: 25 x 5mm. Nominal pathlengths available: 0.015mm to 1.0mm. Construction of mount: aluminum, with polytetrafluoroethylene spacer.

We are supposed to be angry with these boys. "Irtran-2" is our trademark, not theirs. They buy our Irtran-2 optical flats and build cells with them. Anybody who has the skill and the price can buy Irtran optical parts from Eastman Kodak Company, Special Products Division, Rochester 4, N. Y., and build with them.

Irtran-2 optical material is almost completely insoluble in water, which is more than can be said of the rock salt hitherto used for such cells. It can even be boiled in water and detergent to clean out contamination. It can be used in contact with reasonable concentrations of bases and most acids, including the hydrofluoric. Transmittance extends out several microns beyond that of the slightly water-soluble CaF_2. It resists thermal shock much better than BaF_2. It is about as strong as glass. It has a hardness of 354 Knoop.

A cell made out of it does not change pathlength, as does one of NaCl.

Messrs. Warren and Wilks and associates are making and selling cells of Irtran material as fast as we can shoot the Irtran plates to them. We are so angry that we are giving them this advertising for free.

Infiltrated by solid-staters

An oldtimer from the coal pits has been cleaned up with a vengeance, to the accompaniment of long thoughts about "purity" in organic chemistry. (The word is becoming almost useless as a good, all-purpose shibboleth.) You can now buy *Anthracene* as Eastman H480 for $1200 per kilogram.

The prefix "H" stands for hyper-pure. Replace the "H" by "P" for Practical, and the price drops to $6.70 per kg. With "X" prefixed, the price shoots up again to $25.75 for 100 grams because the product is then purified to exhibit a proper blue-green fluorescence. Leave off all prefixes and you get the Eastman Grade at $10.85 for 100g. This is defined as "essentially free from isomers, homologs, and impurities." That "essentially" leaves a little essential room for maneuver. If say 99% of the organic molecules in a bottle are of identical species, most organic chemists would consent to labeling it essentially pure.

But now there has sprung up a breed of organic chemists who work in solid-state physics; or perhaps they are really solid-state physicists extending their realm beyond metals and semiconductors. To them a substance that is only 99% pure is like a pail of garbage. Some of them are even to be found in the Kodak Research Laboratories, which is (or are) where Eastman Organic Chemicals are made.

At their behest *o-Benzoylbenzoic Acid* (Eastman 2242) was cyclized with sulfuric acid to make anthraquinone, that reduced with tin and HCl to anthrone, and *that* reduced with zinc and dilute NaOH to anthracene. This, with much purification and repurification along the way, we call Eastman H480.

For the solid-staters it was only the beginning. They recrystallized it from toluene, got rid of the toluene by a special technique, and zone-refined a dozen times or so. Then by Bridgeman technique in a two-zone furnace they made a large single crystal of the hyper-hyper-pure anthracene. They sandwiched little slices of the crystal between transparent electrodes, applied voltage, and illuminated with an air spark of microsecond duration and very high intensity. They compared current vs. time oscillograms for illumination of the positive side with those for illumination of the negative side. The curves told how long an electron or a hole could drift in the crystal lattice between being set loose by the flash and being trapped by an irregularity or impurity in the lattice. Both electrons and holes showed lifetimes of about 200 microseconds. It is very unusual to have long-lived electrons and holes in the same organic photoconductor. Not only is this very interesting, but long lifetimes permit accurate measurements of the mobility of electrons and holes.

What is happening to organic chemistry?

Whatever is happening, we are continuing the sale of some 3900 Eastman Organic Chemicals from Distillation Products Industries, Rochester 3, N. Y. (Division of Eastman Kodak Company). Write for a copy of List No. 42.

Latest advice on instrumentation film

Background: A photographic material is said to be "fast" if it requires little energy to deliver an image. The term comes from an olden time when portraitists were reducing the duration that the subject had to "hold it" from 5 minutes to 1 minute to a few seconds and on down. Only professors and their brighter students had clear notions of what energy meant. When the photographers did acquire an intuitive grasp of the concept, the physicists kept a step ahead of them by pointing out that the time rate of energy delivery to the emulsion was also important. At this, they were probably accused of pedantry, but unjustly.

The common man came to equate speed with merit in photography. The wise men were sad. "No," they countered patiently, "the faster the emulsion the larger the grains must always be. There is no escape." But there was.

Kodak Royal-X Pan Recording Film, given the proper low-contrast development, is the fastest material we have. This holds true both for hand-camera exposure times and for the very short exposure times of high-speed instrumentation. Royal-X Pan is very good to have when you need every bit of sensitivity you can get, but it is grainier than other Kodak films. Furthermore, its speed advantage over other good Kodak recording films shrinks and disappears altogether for high contrast and very short exposure times.

Very recent advances in emulsion technology have produced the new *Kodak Double-X Panchromatic Negative Film.* For very short exposure times and 8 minutes in Kodak Developer D-19, it is just about as fast as Royal-X Pan Recording Film, but its graininess is much less—on a par with the fine grain and sharpness formerly attainable only in comparatively slow films.

If you want high contrast for very short exposure to green light, *Kodak Linagraph Ortho Film* is your ticket.

All of which tells you nothing of the physical forms of these and other Kodak films for instrumentation, including color film. If you are aware of the omission, you are a person who should send for the capsule-summary sheet "F3-297" from Eastman Kodak Company, Photorecording Methods Division, Rochester 4, N. Y.

Prices subject to change without notice.

Kodak
TRADE MARK

This is another advertisement where Eastman Kodak Company probes at random for mutual interests and occasionally a little revenue from those whose work has something to do with science

WILKENS INSTRUMENT & RESEARCH INC. / P.O. Box 313, Walnut Creek, Calif.
Phone ATlantic 4-7166

AEROGRAPH A-90-P

A NEW STANDARD IS SET FOR GAS CHROMATOGRAPHY INSTRUMENTS

The Aerograph A-90-P, a manual temperature programmed gas chromatograph, is a new version of the well-tested Model A-90-C. It embodies features which make it an outstanding tool for modern day Research and Control work.

Of special interest is the separately heated ovens for the column and detector cell. With this arrangement the column oven may be manually temperature programmed with greatest ease. Isothermal operation is also excellent. Temperatures of the column oven, detector cell, and injector are indicated on the accurate, compensated pyrometer.

Sample collection is very effective. The stainless steel collector tube is controlled by the detector cell temperature preventing sample condensation during passage from the cell to the appropriate collection device.

The detector cell is stainless steel, four-filament with the reference side at atmospheric pressure. It is located conveniently for cleaning or replacing filaments. A built-in D.C., solid state power supply eliminates need for any battery. The efficient Aerograph Flame Detector Kit adapts perfectly to the A-90-P.

- COLUMN OVEN—Variable 350°C with fan for air circulation and cooling.
- INJECTOR—Stainless steel, with adjustable temperature to 400°C.
- DETECTOR OVEN—Cast aluminum with large thermal mass, separately heated to 400°C.
- POWER SUPPLY—Built-in, completely solid state, DC 12 volt, and very stable. No batteries are needed.
- SENSITIVITY CONTROL—Nine step precision attenuation reduces signal by half each step 1 to 500. Accuracy 1%.
- COLUMN INSTALLATION—Easy and rapid with Swagelok fittings. Length to 50 feet.
- MANUAL OVEN CONTROL—Rapid heating and cooling rate.
- AEROGRAPH FLAME DETECTOR KIT—Easily mounted for ultra sensitivity.

The Aerograph A-90-P is recommended as an all-purpose gas chromatograph with a wide range of flexibility. Its small size makes it especially desirable for the crowded bench. Your order by phone or letter will receive prompt attention.

WRITE FOR YOUR FREE SUBSCRIPTION TO AEROGRAPH RESEARCH NOTES FOR SPECIAL DETAILS ON GAS CHROMATOGRAPHY APPLICATIONS.

John Fluke Manufacturing Co., Seattle 99, Washington—*power supply.*

Kahl Scientific Instrument Corp., El Cajon, California—*importer of nuclear electronic gear made by Frieseke and Hoepfner, Germany.*

Land-Air, Inc., San Leandro, California—*survey meters, monitors.*

Landis and Gyr, Inc., New York 36, New York—*importers of G.M. tubes, survey meters, scalers made by Landis and Gyr, Switzerland.*

Nuclear Corporation of America, Denville, New Jersey—*sample preparation device.*

Nuclear Enterprises, Ltd., Winnipeg 21, Manitoba, Canada—*phosphors, scintillators, some detection equipment.*

Nuclear Instruments and Accessories, Inc., New York 10, New York—*distributor of complete line of detectors, handling equipment, and shields; some electronic gear.*

Nuclear Measurements Corp., Indianapolis 18, Indiana—*complete line of detector mounts and counting systems; specialization in monitoring instrumentation for areas, atmospheres; gamma spectrometers.*

Nuclear-Ohio, Inc., Bay Village, Ohio—*detectors, remote pipetter.*

Nucleonic Corporation of America, Brooklyn 31, New York—*complete line of detectors, nuclear accessories, electronic gear.*

Picker X-ray Corp., Nuclear Division, White Plains, New York—*complete line of detectors and electronic gear, much of it designed for training and medical applications.*

Pilot Chemicals, Inc., Watertown 72, Massachusetts—*phosphors and scintillation detectors.*

Planchets, Chelsea, Michigan—*sample preparation supplies.*

Radiation Equipment And Accessories Corp., Lynbrook, New York—*detector crystals, sample preparation and handling equipment, scalers.*

Sharp Laboratories, Inc., La Jolla, California—*low level beta detection system.*

Technical Associates, Burbank, California—*automatic sample changer.*

Technical Measurement Corp., North Haven, Connecticut—*pulse height analyzers and data handling equipment.*

U. S. Nuclear Corp., Burbank, California—*sources, detectors, monitors, scalers.*

Universal Transistor Products Corp., Westbury, Long Island, New York—*survey meters.*

Walkirt Co., Inglewood, California—*counting circuitry.*

BIBLIOGRAPHY

Teachers interested in obtaining federal aid in setting up course work in nuclear fields should consult: U.S.A.E.C., Division of Biology and Medicine, "Grants for Purchase of Equipment in the Fields of Nuclear Technology as Applied to to the Life Sciences, Feb., 1959 (Rev). U.S.A.E.C., Office of Isotopes Development, "Grants for Equipment to be used in Radioisotope Technology Education," Oct. 1, 1959 (Rev).

Next: Chromatographic Equipment.

Chem Ed

Out of the EDITOR'S BASKET

Edited by William G. Kessel

When writing for additional information about new products or for new literature, your inquiry will receive prompt attention if you write on your firm or institution letterhead and mention the Journal of Chemical Education and the date of the particular issue. Pamphlets, booklets and similar literature are gratis unless otherwise specified.

New Apparatus and Equipment

▶ An unusual set of specially-developed, high-precision apparatus will enable laboratories of all types to study sonic phenomena and its applications. Called the "Astro-Lab," this unit has been developed as a "service to science and industry," by Astrosonics, Inc., 190 Michale Drive, Syosset, L. I., New York.

The "Astro-Lab" includes a basic Astrobeam transducer body with a supersonic nozzle designed for operation at Mach. 2, with a gas input of approximately 35 psi. Attached to the nozzle is the oscillator cavity which transduces this high speed gas into sound energy.

▶ SAFE-T-LINE, a new, low-cost Teflon-lined rubber tubing designed to ensure safe flow of highly corrosive laboratory and industrial fluids at temperatures as high as 300°, is now available from the Polytex Division of W. S. Shamban & Co., 11617 W. Jefferson Blvd., Culver City, California.

▶ Fifteen different, inter-changeable, metal vapor and rare gas discharge lamps can now be operated from one universal power supply. These Spectroline Series 1500 lamps provide a broad range of line spectrum through the ultraviolet, visible, and infrared. Since they each emit line spectrum, fine spectral lines can be isolated with appropriate filters. Complete information can be obtained from Spectronics Corp., 20 Corchaug Ave., Manorhaven, L. I., New York, by requesting their Bulletin SP100 on *Line Spectrum and Monochromatic Radiation.*

▶ Recordak Corp., 415 Madison Ave., New York 17, N. Y., has announced the Recordak Starlet, the first low-cost motorized film reader developed for viewing microfilm images. The Recordak Starlet accepts 16 mm microfilm contained in Recordak film magazines, or, with a simple adapter, can also accept microfilm spooled on conventional reels.

▶ A new Calcium Chloride Drying Tube is offered by the Nalge Co., Inc., 75 Panorama Creek Dr., Rochester 2, New York. The "Nalgene" drying tube is designed with one bulb like the usual glass tube. This new design provides a tubulature at the bulb end and tube fitting at the other end. Made of polypropylene, the tube is unbreakable and may be autoclaved.

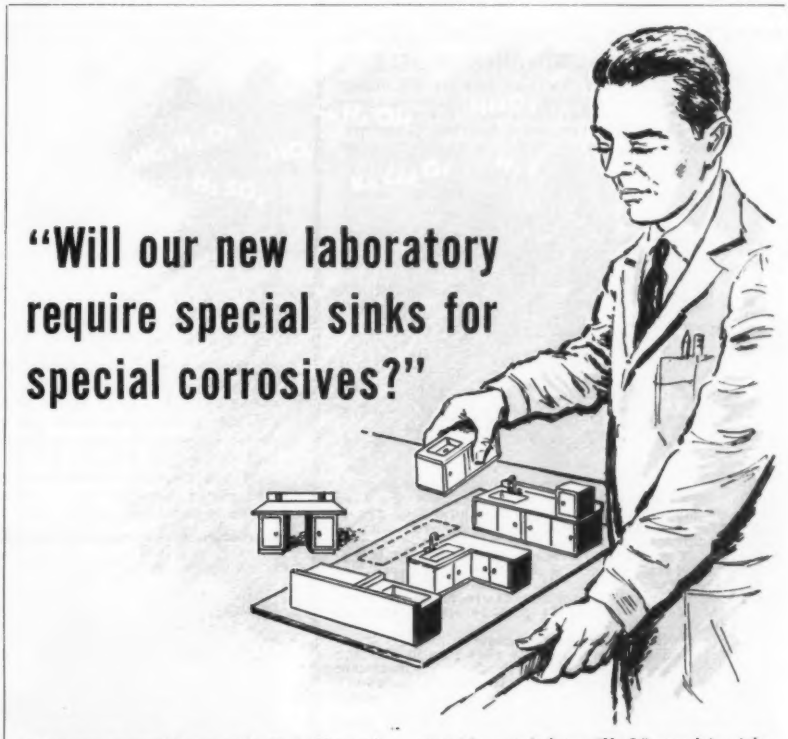
▶ A new, disposable white plastic apron is offered by Busse Plastics Co., 64 E. 8th St., New York 3, N. Y. Waist and bib ties are attached to this lightweight apron of opaque white Impervite vinyl with linen like embossing to retard the flow of drippings.

▶ Hoffmaster Industrial Wipes are made of four plies of "fortified" cellulose and are reported as highly absorbent, soft, and strong whether wet or dry. They are lint free and scratch proof. For complete information write Hoffmaster Co., Inc., Oshkosh, Wisconsin, or Hoffmaster Pacific Co., 1361 E.16th St., Los Angeles 21.

▶ A new portable battery operated Solu Bridge, designated Type RB2, has just been announced by Industrial Instruments, Inc., 89 Commerce Rd., Essex County, Cedar Grove, New Jersey.

▶ Laboratory constant temperature baths designed for a range of −10 to +150°C with a control accuracy of ± 0.01°C are being offered in three models: one with circulating pump for external use and two with full view windows and internal illumination. Mechanical refrigeration is also available. Write the Bayley Instrument Co., Box 538, Danville, California.

(*Continued on page A485*)



Not if you are careful to specify *U. S. Chemical Porcelain Sinks.* For these are the laboratory sinks with time-proven ability to handle all corrosives safely.

Years of continuous service in leading hospitals, universities and industrial laboratories throughout the world attest to the everlasting durability of solid chemical porcelain under all types of corrosive conditions. Acids, alkalies, caustics, solvents —hot or cold, mixed or concentrated—a "U. S." sink handles them all. Commonly used cleaning solutions (such as potassium chromate and concentrated sulphuric acid) which may attack other materials cannot harm "U. S." porcelain sinks. With normal routine rinsing even hydrofluoric acid presents no special problem.

"U. S." sinks offer many excellent advantages. Scratch-resistant, stain-free, smooth gray-glazed surfaces assure a lifetime of beauty. No honing or scouring is ever required. High mechanical strength and superior heat-shock resistance for years of reliable, maintenance-free service.

Your Laboratory Furniture Dealer can give you complete details. See him or write for your free copy of new Bulletin L-8R describing over 50 standard sizes and many styles.

CHEMICAL CERAMICS DIVISION

U. S. STONEWARE
AKRON 9, OHIO

121-0

THE Crescent WIG-L-BUG

WONDER ELECTRIC MORTAR

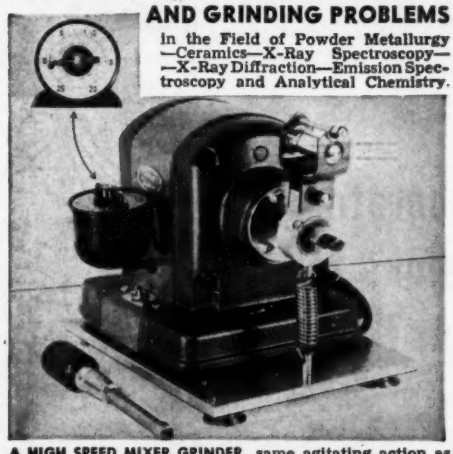
END MIXING—GRINDING DRUDGERY

Using Plastic, Metal or Agate Vials the Wig-L-Bug will become indispensable to you as it has already in hundreds of laboratories in this country and dozens of countries abroad. Use plastic vials for mixing powders or preparing mulls with mineral oil. For grinding hard materials use the hardened tool steel or agate vial. With these you can obtain 200 mesh materials in 2–3 minutes.

For preparing KBr pellets use stainless steel or agate vials. Invaluable in the fields of X-Ray Diffraction, Emission Spectrographic Analysis, X-Ray Spectroscopy, Infra-Red Spectroscopy, Metallurgy, Geology, Oil Research, Aluminum Manufacture, Chemical, Paint and Color Analysis, Ceramics, Foods, Agriculture.

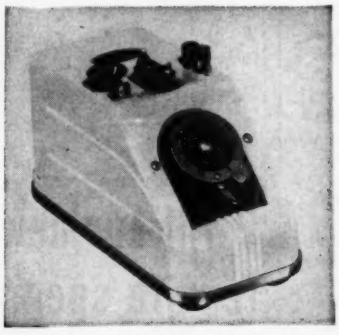
HEAVY DUTY #6—FOR YOUR MIXING AND GRINDING PROBLEMS

In the Field of Powder Metallurgy —Ceramics—X-Ray Spectroscopy— —X-Ray Diffraction—Emission Spectroscopy and Analytical Chemistry.

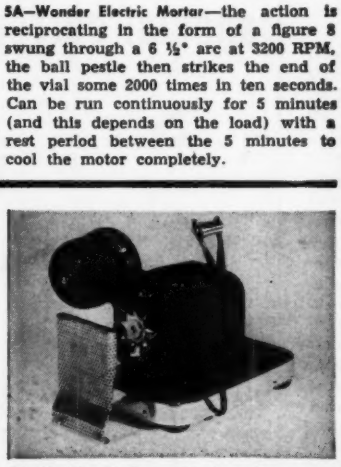


A HIGH SPEED MIXER GRINDER, same agitating action as in small models illustrated. For pulverizing, grinding, crushing, mixing, diluting laboratory samples quickly, consistently and uniformly. In optical emission and X-ray spectrographic laboratories this instrument is ideal for mixing and grinding both samples and standards. Not only is the effort of Mortar & Pestle labor eliminated but results are made more reproducible as consistency in particle size is attained every time.
A ¼ H.P. Split Phase Motor complete with 1 hr. timer and special adapters and arms to hold Plastic, Carbide or Stainless Steel Capsules & Pestles. Approximate weight 40 Lbs. Price $300.00 (No Accessories included). Fin type bearing retainer for longer running intervals available at $15.00 additional. FOB factory.
ACCESSORIES FOR NO. 6 include Plastic Balls & Vials (60 ml) to eliminate metallic contamination. Stainless Steel Vials 6 ml or 10 ml and Rod Pestles or Ball Pestles. Tungsten Carbide 6 ml and 25 ml Vials and Rod or Ball Pestle.

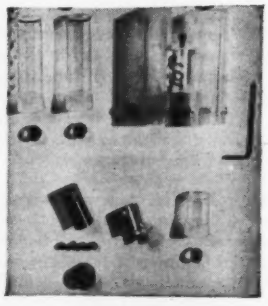
For literature and details write to:



5A—Wonder Electric Mortar—the action is reciprocating in the form of a figure 8 swung through a 6 ½° arc at 3200 RPM, the ball pestle then strikes the end of the vial some 2000 times in ten seconds. Can be run continuously for 5 minutes (and this depends on the load) with a rest period between the 5 minutes to cool the motor completely.



3A—Model with Fan and 1 hour timer—same type of motor and action as 5A Model but this 3A can be run for 20-30 minutes with cooling off periods between to cool the motor.



ACCESSORIES FOR 5A OR 3A WIG-L-BUGS

3113 Adapter, for ⅓" dia. x 1" long vials.
3111 Vial, ⅓" x 1" polystyrene with cap.
3112 Ball-pestle, clear plexiglas, ⅓" dia.
3115 Adapter for ½" dia. x 2" long vials.
3116 Vial, ½" x 2" polystyrene with cap.
3113 Adapter for ½" dia. x 1" long vials.
3114 Vial, stainless steel ½" x 1" with ball-pestle ¼" dia.
3117 Vial, tool steel (hardened) ½" x 1" with steel ball-pestle ¼" dia.
3118 Vial, agate 9/16" dia. x 1 9/16" long 2 ml capacity with agate ball-pestle ¼" dia. (Requires 3115 adapter).

THE WIG-L-BUG HAS REVOLUTIONIZED MIXING & GRINDING PROCEDURES-A TREMENDOUS TIME SAVER, CONSISTENTLY UNIFORM RESULTS. AN INDISPENSABLE LABORATORY MORTAR MIXER

CRESCENT DENTAL MANUFACTURING CO.

1837 So. Pulaski Road • Chicago 23, Ill.

Out of the EDITOR'S BASKET

▶ A new, compact, higher-capacity Model K-5 integral air pump and motor providing 27" Hg vacuum continuous, 15 pounds pressure and 12 cfm volume, is announced by Leiman Bros., 102 Christie St., Newark 5, New Jersey.

▶ Blue M Mechanical Convection, horizontal airflow Dry-type Incubators, with full-size glass observation panel, double-wall construction, built-in copper cooling coil, and Power-O-Matic 60 Control System, provide features excellently adapted for equipment restricted to a particular "scope" of operation. Contact Blue M Electric Co., 138th and Chatham St., Blue Island, Illinois, for additional details.

▶ "Swish Aerosol Elektrokleen," an aerosol cleaning compound for a wide variety of uses in cleaning electrical equipment, electronic components, typewriters and office machinery, power tools, fans and ducts, is now available with a removable extension tube for cleaning hard-to-reach places. "Swish Elektrokleen" is produced by Montgomery Chemical Co., Jenkintown, Pennsylvania.

▶ A newly designed Electronic Resistance Thermometer has been introduced by the Manostat Corp., 26 N. Moore St., New York 13, N. Y. It eliminates the time-consuming calculations normally necessitated with high precision resistance thermometry and gives direct digital reading of temperature from minus 100°C to plus 900° C, with 0.25°C or 0.2% accuracy (whichever is greater).

▶ To meet the growing demand for more safe processing ovens in hazardous atmospheres, also where safety from destruction by overheating of the processed material is of utmost importance, "Modernlab" has designed a new safety control system, unique with this type of equipment. Write Modern Laboratory Equipment Co., Inc., 1809–11 First Ave., New York 28, N. Y.

▶ A new "Tygon" Protective Coating, the Tygon AV Series, specially designed for use with airless spray equipment, has just been announced by The Coatings Linings Division of The U. S. Stoneware Co., Akron 9, Ohio.

New Literature

● New *Bulletin #167* just released by Barnstead Still and Sterilizer Co., 168 Lanesville Terrace, Boston 31, Massachusetts, describes its complete line of tin-lined and tin-coated draw-off faucets. The use of tin prevents metallic contamination and makes these faucets ideally suited for use with distilled or demineralized water distribution systems.

● A new Wilkens-Anderson *Chemical and*

(*Continued on page A488*)

Convenient • Efficient • Economical

Welch **TRIPLE-BEAM TRIP-SCALE**

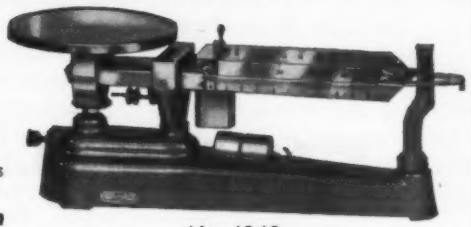
SPEEDY, ACCURATE WEIGHING

Stainless Steel Beam and Pan

• *Large Capacity- 1610 Grams*

With Extra Weight-2110 Grams

• *Sensitivity to 0.1 Gram*



No. 4048

3 Graduated Scale Levels for easy reading. Riders move easily. Hard, Cobalt Knife Edges maintain true edge indefinitely.

Grooved Agate Bearings are protected against damage, yet highly resistant to corrosive action of laboratory fumes.

One-piece Beam Construction—Silver-Gray Hammerloid Finish Rapid Zero Setting—Beam Arrest for faster weighing.

No. 4048 LOW FORM-PRICE, WITH TWO EXTRA WEIGHTS...$21.00
No. 4048C PLASTIC COVER, For 4048 .....Each, $1.10
No. 4048W EXTRA WEIGHT. For increasing the capacity of No. 4048 to 2110 grams.....Each, $1.45

Write for Circular

THE WELCH SCIENTIFIC COMPANY

—ESTABLISHED 1880—

1515 Sedgwick Street, Dept. D-1, Chicago 10, Illinois, U. S. A.

Manufacturers of Scientific Instruments and Laboratory Apparatus

Instant, Positive, GAS DETECTION...

with the BROTHERS test proven Detection Kit

- Sensitive well below the mac range*
- Consistant results
- Easy to use
- Wide choice of tubes

$ 85.00
COMPLETE with pump, remote sampler and one hundred tubes in sturdy leather case.

Don't take chances with poisonous and deadly fumes. This easy-to-use, precision instrument will tell you when dangerous fumes are present . . . down to a few PPM. Send for complete literature.

* MAXIMUM ALLOWABLE CONCENTRATIONS for exposure during an eight hour day adopted at the 22nd annual meeting of the American Conference of Governmental Industrial Hygienists.

BROTHERS CHEMICAL

BROTHERS CHEMICAL CO., INC.

ORANGE, NEW JERSEY

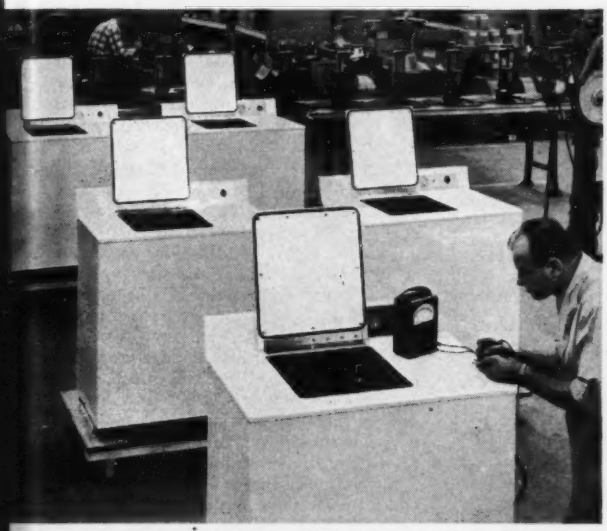
FISHER STOCKS WHAT

Depend on fast delivery from Fisher's 14 convenient branches. Newest is in Boston, boosting Fisher's total warehouse space to more than three-quarters of a million square feet. In each strategically located branch, skilled crews fill your order carefully, ship it promptly.

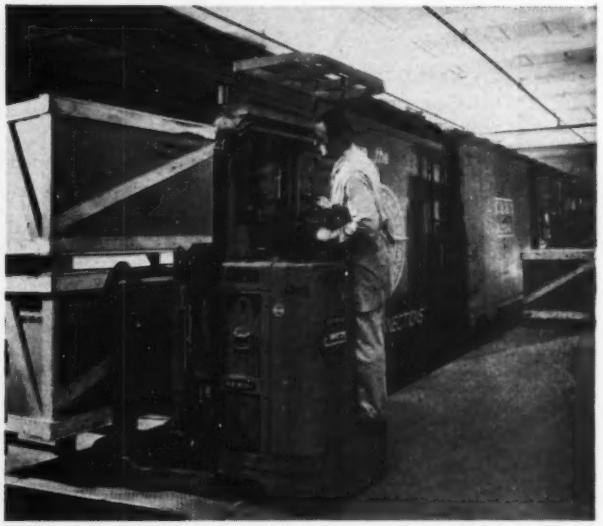
T YOU NEED!

WELL-STOCKED shelves at Fisher Scientific's new Boston branch (left) attest to the huge Fisher inventory: over 20,000 different instruments, appliances, glassware items and furniture units . . . over 7000 different chemicals. Each Fisher branch maintains its own comprehensive stocks so one order can bring your laboratory everything it requires . . . a **single source** that saves you time and money.

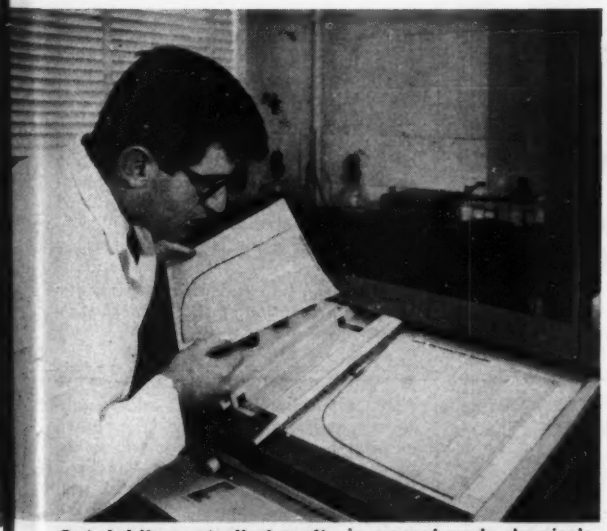
Comprehensive stocks are just one feature of the Fisher organization . . . others are noted below. In total, they are the reason Fisher Scientific is a leader in the field of laboratory instrumentation and reagent manufacture.



Reduce "housekeeping" time, costs. New Standard Washer gets glassware sparkling clean . . . quickly, economically, safely. It was developed for small labs by Fisher engineers who pioneered much of the apparatus you use.



Speed lab expansion, avoid delays. Order Fisher Unitized Furniture that's quickly available from stock. And take advantage of Fisher's many other services such as lab planning, free technical information, expert instrument repairs.



Get rigidly controlled purity in reagent-grade chemicals, "spectranalyzed" solvents from Fisher. In its modern plant, Fisher makes these and other high-purity chemicals under strict controls to assure uniform quality.

Want to have more facts about how Fisher can help you? Details in free, data-packed bulletins. Clip, fill out and mail coupon to Fisher Scientific Company, 109 Fisher Building, Pittsburgh 19, Pa.

Fisher Scientific Company
109 Fisher Building
Pittsburgh 19, Pa.

Please send me the following information:

- ☐ "This Is Fisher"
- ☐ Fisher Glassware-Washers
- ☐ Fisher "Spectranalyzed" Solvents
- ☐ Fisher "Unitized" Furniture

Name_____ Title_____
Please Print

Company_____

Street_____

City_____ Zone_____ State_____

G-178

FISHER SCIENTIFIC

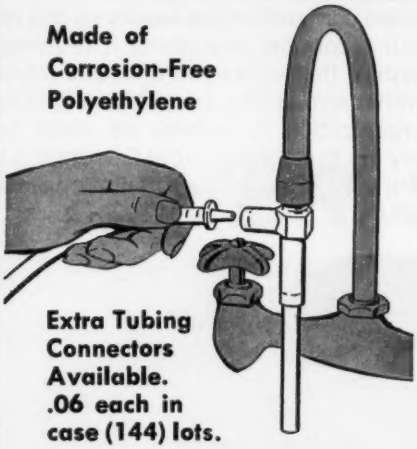
World's Largest Manufacturer-Distributor of Laboratory Appliances & Reagent Chemicals

Boston • Chicago • Fort Worth • Houston • New York • Odessa, Texas
Philadelphia • Pittsburgh • St. Louis • Washington • Montreal • Toronto

Always Specify PIONEER Labware For Finest Quality

Pp

Made of Corrosion-Free Polyethylene

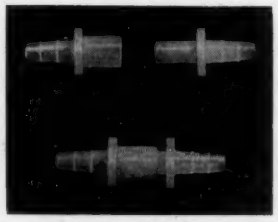


Extra Tubing Connectors Available. .06 each in case (144) lots.

FILTER PUMP

Operates on water pressure from 11 lbs. up. All-polyethylene. Integral check value not affected by fumes or corrosive filtrate. Takes up to $^3/_8$" tubing—connects and disconnects instantly. Has $^3/_8$" IP male thread faucet connection.

Priced at $1.30 Each in case (72) lots.



Priced .25 ea. in case (72) lots.

QD CONNECTORS

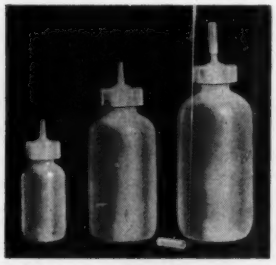
A quick disconnect flexible tubing connector. Designed particularly for vacuum applications. Also useful for connecting water lines, manometers, etc. Light in weight and may be used safely in apparatus set ups. Fits tubing of $^5/_{16}$" to $^3/_{16}$" ID.

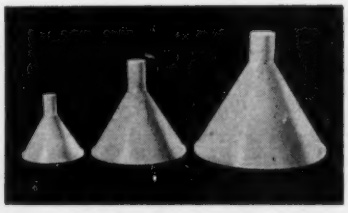
DROPPER BOTTLES

With New Improved Caps

Screw-on cap effects tight seal permanently. Drops are small and uniform. By far the best available for laboratory use.

Six sizes, priced from .12 ea. in case (72) lots.





POWDER FUNNELS

Parallel stem minimizes bridging of powder. No airlock, 60° angle. 65, 100 & 150 MM diameters. Priced from .32 each in case (72) lots.

Send for catalogue of complete line of unbreakable polyethylene labware—sold through leading supply houses.

PIONEER PLASTICS, Inc.
Box 8066 Arlington Branch, Jacksonville 11, Florida

Out of the EDITOR'S BASKET

Laboratory Supply Catalog is now available for schools. The new 486 page catalog includes an expanded chemicals section in addition to the apparatus and equipment listings. Alphabetical arrangement and clear presentation helps user save time in ordering. Schools using or considering the Semi-Micro methods will find in this catalog a complete line of Semi-Micro items. For a free copy of this catalog, write Wilkens-Anderson Co., 4525 W. Division St., Chicago 51, Illinois.

● A new 96 page catalog, describing more than 250 instruments, counting systems, radionuclides, and nuclear accessories has been announced by Nuclear-Chicago Corp. of Des Plaines, Illinois.

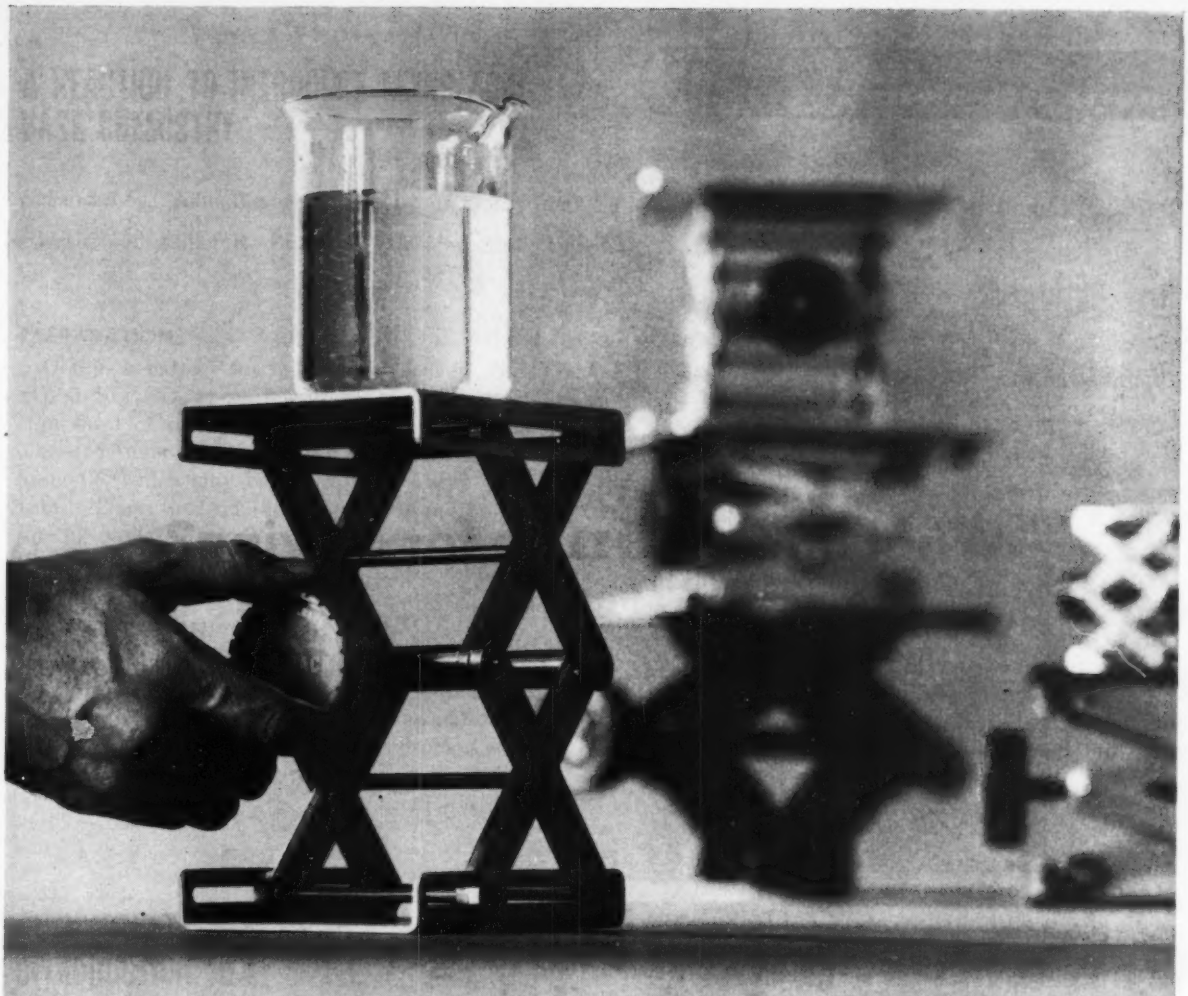
Principal new products include: 1. Automatic sample changers for beta and gamma samples on large diameter planchets or in test tubes. 2. Manual and automatic liquid scintillation detectors. 3. Integrated, modular research-type instrumentation with in-line digital readout of time and count. 4. Laboratory monitors—both AC and battery operated. 5. Improved scintillation detectors. 6. Expanded line of G-M tubes and neutron sensitive BF_3 counters. 7. Neutron Generators manufactured by Nuclear-Chicago's new subsidiary, Texas Nuclear Corp. 8. Radioactivity training systems for students. 9. License-exempt radionuclides for training purposes. 10. Personnel protection devices, including a new film badge service and dosimeters.

Copies of the new *General Catalog S* are available to educators, biochemical and industrial researchers on request.

● Texas Gulf Sulphur Co., 75 E. 45th St., New York, N. Y., producer of crude sulphur as mined by the Frasch Hot Water Process, has prepared a revised edition of *Modern Sulphur Mining*. This edition updates statistical data and latest developments in both production and distribution of this essential commodity. Much information is contained within its pages that can be of value to teachers when lecturing on the chemistry of sulphur.

Copies can be obtained by writing the company, attention of the Sales Department.

● Fashion Seal Uniforms, 63 New York Ave., Huntington, New York, manufacturers of uniforms for the hotel, hospital, professional and industrial fields, has recently completed a 20 page handbook devoted to uniforms of lint-free, acid resistant synthetic fabrics. This book is a complete guide to proper selection usage and care of work apparel with emphasis placed on the uniforms' function in white rooms. It contains actual fabric swatches and charts pointing out the various benefits that the different families of synthetic fabrics offer.



THE CENCO LAB JACK

Imitation is the sincerest form of flattery and the Cenco Lab Jack has been overwhelmed with it. While some who have followed offer sound design, or others decent quality, none (as yet) has equalled Cenco's design and quality at the same price.

Developed in collaboration with Dr. Aaron B. Lerner of Yale University, the Cenco Lab Jack's simple, efficient design and precision construction are still its outstanding features. It will hold 100 lbs. easily, with complete stability at all elevations between 3 and 10¼ inches. Its scissors action permits steady, level, and quick raising or lowering—a feature especially noticeable when maneuvering fragile glassware.

With over 25,000 in use throughout the world today, we find only one trouble with the Cenco Lab Jack. It lasts too long.

NO. 19089-001-Cenco—Lerner Lab Jack **$34.00**

CENTRAL SCIENTIFIC *A Division of Cenco Instruments Corporation*
1700 West Irving Park Road, Chicago 13, Illinois

Mountainside, N. J.
Montreal
Santa Clara
Somerville, Mass.
Toronto
Los Angeles
Birmingham, Ala.
Ottawa

cenco

Vancouver
Houston
Cenco S.A., Breda, The Netherlands
Tulsa

What does Olin do for a living?

A lot of things. Some of them might surprise you. Read this.

Olin conceives new products at a rate of no less than one a week. Some appear under our own name. Others bring fame to our customers.

Did you know that Olin pioneered liquid chlorine and synthetic ammonia in the U.S.? Is a leader in agricultural chemicals and synthetic detergent builders? Makes the hydrazine derivatives used as missile fuels? Some of the work of our **CHEMICALS DIVISION**

Common clay is now anything but "common." In the lab, we recently developed an economical process to convert clay into—of all things—alumina. Stronger metals, new alloys, and metal sources that would have made alchemists scoff in disbelief, are now being pioneered by our **METALS DIVISION**

Our organic intermediates—those polysyllabic tongue twisters only chemists can pronounce easily—are used in the manufacture of many new "wonder" plastics. We recently developed smokeless Ball Powder® with many immediate uses, and many more astonishing potentials. New and better explosives, detonators and blasting caps are challenges in Olin's **ORGANICS DIVISION**

Our research teams are probing for new films to keep foods fresh longer. We work with packaging materials from cellophane to kraft paper, corrugated boxes to lumber. The seemingly incongruous quests for crisper potato chips, lighter weight printing papers and more effective cigarette filters are all part of Olin's **PACKAGING DIVISION**

In the very research center where penicillin was first crystallized, scientists now probe for a B_{12} antagonist to arrest cancer. On any given day, 150 of our drugs or new dosages may be undergoing clinical tests throughout the world. From Olin's **SQUIBB DIVISION**

Olin even works on your leisure, with sporting arms and ammunition. We discovered a new way to make a shotgun barrel by winding 500 miles of Fiberglas® around a thin steel liner. It is superior to all-steel barrels on many counts. Ammunition research led to development of powder-actuated tools for faster, stronger fastenings in construction. At our **WINCHESTER-WESTERN DIVISION**

Olin products are sold in virtually every free country in the world. Sales, service and manufacturing for overseas markets are the responsibilities of our **INTERNATIONAL DIVISION**

Olin Mathieson Chemical Corporation, 460 Park Avenue, New York 22, N. Y.

DETACH PAGE BY CUTTING ALONG THIS LINE—INDIVIDUAL DEMONSTRATIONS MAY BE CUT APART AND PASTED ON 5 X 8 CARDS

A REACTION TO INTRODUCE LEWIS ACID-BASE CHEMISTRY

A Chem Ed TESTED DEMONSTRATION

Submitted by: John Baxter, University of Florida and Carleton Spear, Deerfield, New Hampshire

Checked by: Julian R. Brandou, Michigan State University

PREPARATION

Obtain a battery jar or 1000 ml beaker, source of SO_2 and/or CO_2 gas, a few grams of soda-lime, and a thin sheet of rubber (dental dam or rubber balloon). The soda-lime should be stoppered in a thin-walled ampoule, which may be blown from a soft glass test tube. Place the soda-lime container in the battery jar, fill with CO_2 or SO_2, and cover with the rubber sheet; fasten it firmly in place with string, rubber band, or tape.

DEMONSTRATION

Shake the jar violently so as to break the thin-walled glass container permitting the gas to come in contact with the soda-lime. Observe the deformation of the rubber covering as the gas pressure drops due to the reaction with the base.

REMARKS

The equation for the reaction may be represented as:

$$CaO + SO_2 \rightarrow SO_3^{--} + Ca^{++}$$

After cutting the neck from a large paddle shaped balloon, the remainder can be used to close the mouth of the battery jar without additional fastenings.

For those who do not have glass blowing facilities, the soda-lime may be placed in a test tube of appropriate size and stoppered. The stoppered test tube is then placed in the jar before covering with the rubber. The rubber covering is sufficiently flexible to permit the operator to hold the test tube and shake the soda-lime out of the tube with results similar to those described above.

INTRODUCTION TO LE CHATELIER'S PRINCIPLE

A Chem Ed TESTED DEMONSTRATION

Rewritten and adapted from: G. Fowles, "Lecture Experiments in Chemistry," Basic Books, Inc., New York, 1959, by Julian R. Brandou, Michigan State University

Checked by: Joseph E. Bowles, Traveling Science Teacher Program

PREPARATION

Fill a 1 or 2 liter round bottom flask with dry HCl gas at room temperature. Provide a one hole stopper on the stem of a 110° thermometer, wrap the bulb with several layers of gauze and tie firmly. Add 25 ml concentrated HCL solution to a smaller flask, arranged for heating.

DEMONSTRATION

Wet the gauze around the thermometer bulb, read and record the temperature, insert in HCl gas and observe the rise in temperature of 40° or more.

Warm the concentrated HCl solution in the small flask until vapors are easily noted by breath or other means.

REMARKS

This large temperature change is quite dramatic. Since the solution of gaseous HCl in H_2O is an exothermic reaction, heating an aqueous solution decreases the solutility of the gas. This demonstration may serve as an introduction to a discussion of Le Chatelier's Principle.

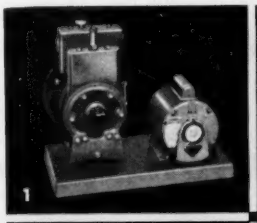
DETACH PAGE BY CUTTING ALONG THIS LINE—INDIVIDUAL DEMONSTRATIONS MAY BE CUT APART AND PASTED ON 5 X 8 CARDS

QUIET - VIBRATIONLESS - ALL-PURPOSE

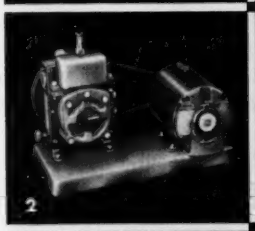
WELCH DUO-SEAL® VACUUM PUMPS

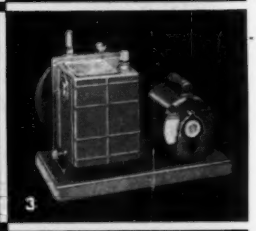
actually improve with use

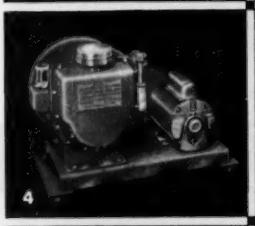
Advanced Design • Remarkably Quiet • Long-Life Performance

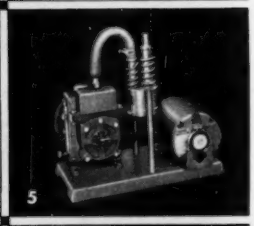


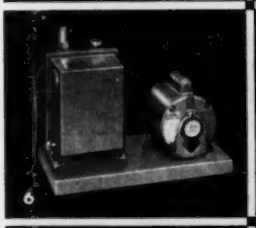
The complete line of Duo-Seal Vacuum Pumps is shown here. Descriptions and prices below.

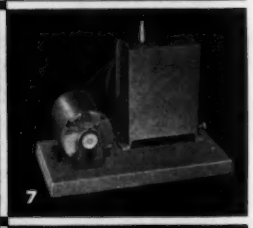


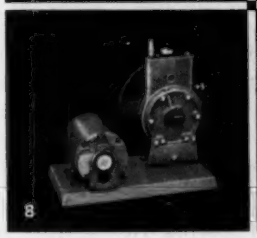


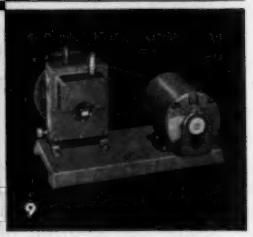












Whether it's in the laboratory, on a busy production line, in a classroom, reduced noise level means greater efficiency, higher quality work. Duo-Seal Vacuum Pumps are *quiet*. Welch engineers took noise and vibration out of the vacuum pump right on the drawing board. The result is a pump that runs as quietly as an electric motor.

Quite operation means greater efficiency.

Quiet, vibrationless operation means pumps that run smoothly year after year with virtually no maintenance beyond a periodic oil change. Duo-Seal pumps, built to close tolerances, actually improve with use, the seal and vanes become more highly polished and the fit more perfect.

There is a Duo-Seal pump available for almost every purpose, for every budget, from noncritical classroom problems to most exacting high-vacuum industrial-production and laboratory vacuum requirements.

Welch Pumps are best because: Every pump is triple tested. Specified performance guaranteed. Lowest cost per year of use. Highest vacuum of any mechanical pump. Quietest mechanical pump made.

For complete specifications, request our pump catalog.

For every vacuum requirement.

1. No. 1405 (2 speeds available) two-stage, No. 1405H. 0.05 micron, 33.4 liters per minute. $230.00. No. 1405B. 0.1 micron, 58 liters per minute. $225.00.

2. 1400B—two-stage. 0.1 micron, 21 liters per minute. $133.00

3. 1402B—two-stage, vented exhaust, 0.1 micron, 140 liters per minute. $310.00

4. 1397B—two-stage, vented exhaust, 0.1 micron, 425 liters per minute. $645.00

5. 1392—mechanical and diffusion pump assembly, two-stage (each element) 0.001 micron, 600 liters per minute. (at 0.1 micron) $300.00

6. 1403B—single-stage, 5 microns, 100 liters per minute. $245.00

7. 1404H—Wegner Pump single-stage, 20 microns, 33.4 liters per minute. $150.00

8. 1406H—single-stage, 5 microns, 33.4 liters per minute. $150.00

9. 1410B—Wegner Pump single-stage, 20 microns, 21 liters per minute. $100.00

THE WELCH SCIENTIFIC COMPANY

ESTABLISHED 1880

1515 SEDGWICK STREET; DEPT. D, CHICAGO 10, ILLINOIS, U.S.A.

Manufacturers of Scientific Instruments and Laboratory Apparatus

DUO-SEAL PUMP OIL is a must to keep your Duo-Seal vacuum pumps operating at highest vacuum and efficiency. A chemically-stable, low-vapor-pressure product, Duo-Seal Oil is produced according to the most exacting specifications. $0.90 qt. $2.65 gal.

Chem Ed

EDITORIALLY SPEAKING

The title of the first article in this issue asks one question but raises several. How many times have teachers of freshman chemists been asked this question in one form or another! It is typical of the kind that flies free before the sophistication born of a little information clips the wings of curiosity and imagination. Our guess is that the number of times it is asked far exceeds the number of times it gets a satisfactory answer. The article we are featuring should help that situation. It is an elegant example of how to treat a profound theme with uncluttered illustrations in simple, direct language.

Even if teachers do not have to scratch their heads over this specific question, there are implications in this discussion which are real puzzlers. Is "entropy" a bad word to use in an elementary chemistry course? The survey reported in the May issue (page 256) put "entropy" next-to-the-last in the list of topics considered important by teachers of college general chemistry. The word appears in the indexes of only three of three dozen recent textbooks.

Is this situation inevitable? Do we have to get so much essential information into the students' heads *before* we dare introduce concepts of such far-reaching practical and theoretical significance as free energy and entropy? Most of the time we use the excuse that this is "too advanced" and will only confuse the beginner. This may be true, but we suspect that what we really mean is that we ourselves do not understand the concept thoroughly enough to expose our ignorance to the penetrating inquiry of a thoughtful, bright beginner. Here is another example of the situation constantly confronting the chemistry teacher: he cannot teach from the surface of his store of information. He must have not only a depth of knowledge but also the courage to dig deep on occasion. We hope the present article can serve to add depth to some teachers' information and to stand as an imaginative example of courageous teaching.

Chemistry professors should disturb themselves with another question. This emerges from the fact that while authors of elementary chemistry textbooks ignore "entropy," those writing books for use in "physical science" courses for non-majors do not. Four of the five newest texts not only index the term but give a very accurate appraisal of its significance. To be sure, they do not talk about "$2.302\ R \log W$," but they do help the student to realize that "Entropie stebt einem Maximum zu." At least *some* of the awesome mystery of the second law of thermodynamics is dispelled. Courses taught from such texts can make it possible for these students to read the *Scientific American*—or even the Sunday supplements—where cosmology, biogenesis and energy-for-the-future are becoming more and more common topics.

Should this kind of thinking big thoughts be denied students in a beginning chemistry course? Should they have to sit in embarrassed puzzlement when in a social science class the professor asks what Carl Becker means when he introduces a chapter in his "Progress and Power" with the statement "dS/dt is always positive"; should the pre-medical student never hear of entropy until Blum's "Time's Arrow and Evolution" appears on a reading list in an advanced biology course? This often happens, and teachers of general chemistry should pause for reassessment.

We are not advocating substituting a study of thermodynamics for general chemistry, but we are suggesting that far-reaching correlative principles not be ignored entirely. Proper introduction can be done in the "vocabulary" of general chemistry to give students some very powerful "grammar" to use all through their scientific education. Furthermore, when such terms as "entropy" do get tossed around in a social science or philosophy context, familiarity with them as scientific concepts will do more than merely relieve the embarrassment of chemistry students. Not infrequently they have to be able to recognize the fallacious basis or tenuous application of analogies to scientific concepts taken out of context. If students in science courses for non-majors can be provided this information why not educate chemists for intellectual life beyond the ivory laboratory too?

The cover

Wooster student Don Barnes is amazed. He thought it never could be done, but the article featured here decreased much of the entropy made positive by the editor's attempt to teach him thermodynamics. With all those translational shelves available what N atoms wouldn't be anthropomorphically happy and spontaneously dissociate at high temperatures?

George E. MacWood
and **Frank H. Verhoek**
The Ohio State University
Columbus

How Can You Tell Whether a Reaction Will Occur?

De chemiske Processer have saaledes een foelles Egenskab, en almindelig Charakteer, nemlig den, at enhver chemisk Proces, naar den betragtes i sin Heelhed og i sin Reelhed, ledsages af en Varmeudvikling.[1]

Tout changement chimique accompli sans l'intervention d'une energie étrangère tend vers la production du corps ou du système du corps qui degagé le plus de chaleur.[2]

Every teacher of chemistry knows that the answers of Thomsen and Berthelot to the question in the title are not correct. When we discuss this with our students, however, we sometimes find ourselves a little uncertain how to show them why it is not correct and to explain what is correct. This paper is another in the many which have been written in the last 80 years attempting to clarify this question.

Processes Which Occur with Decrease in Energy

The difficulty arises partly from the fact that the statements quoted seem so intuitively reasonable, on the basis of our knowledge of common mechanical systems. Everyone knows that a ball at the top of an incline will roll downhill. The ball moves from a position of high potential energy to a position of low potential energy; it can be moved back only by expenditure of work on the system. From this observation, and observations on many similar systems, one concludes that the more stable state is the state of lower potential energy.

Potential energy is measurable only by transforming it to some other form of energy. This is also true of chemical energy, and it is a short step (with the example before us of the ball rolling downhill, reaching the state of lowest energy) to conclude that chemical reactions also proceed in such a direction as to reach the state of lowest energy. On this basis reactions would go of themselves in such a direction as to evolve energy, just as a ball at the top of a hill, if released, will roll down. A ball at the bottom of a hill will not however, of itself, absorb energy and roll uphill; and we would predict that no chemical reaction could, of itself, as a result of simple mixing of the reagents, take place with absorption of energy.

This prediction—that only exothermic reactions take place—is in accord with many experimental facts. Most common chemical reactions *do* occur with evolution of energy. It is no wonder that Thomsen and Berthelot saw the requirement of energy evolution as a law of nature. Thomsen, in fact, was so convinced of its truth that he upbraided Berthelot for failure to give him credit for his prior statement of the "law"![3] Qualitative observations seem to show not only that reactions take place with evolution of energy, but that they are more vigorous, the greater the amount of energy released. As pointed out long ago by Sackur, the heat of formation of a compound is in general greater the more easily the compound forms.[4] In oxidation processes, for example, one finds that the alkali metals, which have a high heat of oxidation, oxidize vigorously on exposure to air at ordinary temperature, while carbon, with a lower heat of oxidation, must be heated. The heavy metals oxidize with still more difficulty, in accord with the still lower heats of reaction for these elements. Many similar cases could be cited, all contributing to the impression that the evolution of energy is the controlling factor in chemical reactions.

One need not search long however, to find examples of endothermic reactions. A familiar one is the reaction of water gas production by passing steam over hot carbon.

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \qquad (1)$$

Here the endothermic character of the reaction dictates the engineering process. The cooling effect of the reaction is intermittently compensated for by blowing air into the reactor to reheat the coke by partial combustion. In this reaction the energy of the products, carbon

[1] "Chemical processes thus have a common property, a general characteristic, namely this, that every chemical process, when examined in its entirety, is found to be accompanied by an evolution of heat," JULIUS THOMSEN, in his lecture "Om de chemiske Processers almindelige Charakteer og en paa denne bygget Affinitetslaere" presented before the meeting of the Danish Academy of Sciences on March 22, 1861. ("Oversigt over de Kongelige Danske Videnskabernes Selskabs Forhandlinger i Aaret 1861," pp. 100–134.) In this lecture Thomsen refers to his earlier publication in the Academy's "Skrifter," series 5, volume 3 (1853). This was shortly published serially in German in *Annalen der Physik*, **88**, 349–362; **90**, 261–288 (1853); **91**, 83–103; **92**, 34–57 (1854); and the German statement "Jede einfache oder zusammengesetze Wirkung von rein chemischer Natur ist von einer Wärmeentwicklung begleitet" (*Ann.*, **92**, 36 (1854)) is usually quoted.

[2] "Every chemical change carried out without the intervention of energy from an outside source tends toward the production of the substance or group of substances which release the most heat," M. BERTHELOT, in *Annales de chimie et de physique* [5], **4**, 52 (1875). Berthelot's earliest statement appears to have been in his appearance before the Academy of Sciences on March 4, 1867; "*Toute reaction chimique, capable de donner lieu à un dégagement notable de chaleur, se produit nécessairement et d'une manière directe, toutes les fois qu'elle satisfait aux conditions suivantes, dont la première seule est fondamentale: 1. la reaction est comprise dans la categorie de celles qui atteignent leurs limites dans un temps trèscourt, à partir de leur commencement*," *Compt. Rend.*, **64**, 413 (1867).

[3] *Berichte*, **6**, 425 (1873). Berthelot's reply, *Bull. Soc. Chim.*, **19**, 485 (1873).

[4] SACKUR, OTTO, "Textbook of Thermochemistry and Thermodynamics," translator, G. E. GIBSON, Macmillan and Co., London, **1917**, pp. 127–128.

monoxide plus hydrogen, is greater than the energy of the reactants; the ball, so to speak, has moved uphill. It did this of itself; our part in the process was only to make energy available if the steam and coke wished to make use of it to form carbon monoxide and hydrogen. No work was done on the system in order to cause the energy to be absorbed; in fact, the system produced work, expanding against the atmosphere in the formation of two moles of product gas for each mole of reactant steam which disappeared.

The energy change is thus not a completely reliable quantity for deciding whether a chemical reaction will occur, although it *is* reliable when predicting what a ball will do if placed on an inclined surface.

Processes Which Occur with Increase in Randomness

To explain how an endothermic reaction can take place, let us first consider a process which proceeds of itself with *no* energy change. Let us take a liter of helium and a liter of neon, and connect the two containers by means of a large valve (Fig. 1).

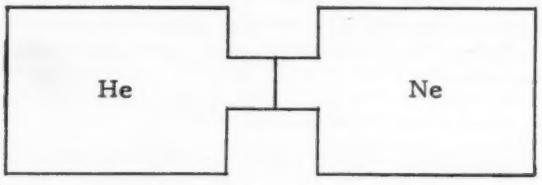


Figure 1. Helium and neon in the separated initial state.

If we open the valve, the two gases will mix, until the helium and neon are distributed evenly between both containers. This process takes place with neither evolution nor absorption of heat; hence there is no question of a decrease in energy to a lower level. Some driving force other than the decrease in energy must be involved here; there must be another property which determines whether a "reaction" can take place. The reverse of the process of self-mixing—to have all the helium in the mixture gather itself into one vessel and all the neon in the other—will not take place of itself. In this respect the system is similar to that of the ball at the bottom of the hill which will not, of itself, roll to the top.

We have then two different processes—the ball rolling down hill and the gases mixing—which occur spontaneously, i.e., of themselves. In one we explain the behavior in terms of a change to a state of lower energy. How shall we explain the other?

Note that the final condition of the two gases, after mixing, is a more random one than the initial condition; there is less order in it than when the two components are separate and pure. If the mixture were before us, we would say that it was unlikely or improbable that the components would separate of themselves; hence we could say that the mixed state had a greater probability of existence than the unmixed state. The driving force in this process is the tendency to go to the most probable, the most random state. We find this to be a general rule: a system which can go from one state to another without a change in energy will adopt that state which has the greater degree of mixing, the higher probability, and the more randomness.

The measure of the mixing, the probability, and the randomness is called the *entropy*. The entropy, S, of a mole of substance in a particular state (that is, under specified conditions of temperature, volume, and pressure, and in a known state of aggregation, i.e., solid, liquid, or gas) is proportional to the logarithm of the probability of finding the substance in that state.

$$S = 2.303R \log W \qquad (2)$$

Here R is the gas constant (calories per degree per mole; hence S as defined is the molar entropy in calories per degree per mole) and W is the probability. For this purpose we may consider the probability to be measured by the number of ways of reaching the state in question. For example, if we had a cubic die on which five faces were marked A and one face was marked B, the probability that in a single throw an A would turn up is five times as great as that a B would turn up, because there are five ways of obtaining an A but only one way of obtaining a B. Another way of saying this is to say that the more probable state has fewer restrictions than the less probable. In obtaining a B, the less probable state, we are restricted to one way in which the die must land, but for an A we have five ways. Similarly the probability of the unmixed state in the example of neon and helium is lower than that of the mixed state because in filling the container in the unmixed state we are restricted to placing all neon molecules in the right-hand half, and all helium molecules in the left-hand half. In the mixed state, however, we have a choice of two positions for the neon molecules, which now have both the left-hand and the right-hand half available to them, and similarly for the helium molecules. We shall find in general that the probability—and hence the entropy—is higher the more places there are to put the molecules of the system under consideration.

Processes in Which Both Energy and Randomness Change

We see that there are two driving forces for natural processes: a tendency to adopt the lowest energy, and a tendency to adopt the highest entropy. If there is no change in energy, the second is the controlling factor. If there is no change in entropy, in randomness, the first is the controlling factor. What is the situation when both the energy and the randomness change, as is the usual case in a chemical reaction?

The two changes are more or less independent of each other. In some cases the more probable state may be a state of lower energy, but in other cases the more probable state is the state of higher energy. When the latter applies, the change toward the more probable state is opposed by the need to increase the energy of the system. The system will go in the direction of the larger change if the two changes are opposed; thus the driving force in such a case is the difference between the increase in energy and the increase in randomness.

The net driving force for a proposed process depends upon the *difference* between the two quantities

(energy in final state minus energy in initial state)
and
(randomness in final state minus randomness in initial state)

If the two quantities are exactly equal, the difference is zero, and no change at all occurs; in chemical terms,

the system is at equilibrium.

For convenience we call the net driving force a change in free energy, as if there was a special kind of energy—the free energy—associated with the initial and final states, so that we can write

(free energy of final state − free energy of initial state) *equals* (energy in final state − energy in initial state) *minus* (randomness in final state − randomness in initial state) (3)

or, in symbols,

$$[A_{\text{final}} - A_{\text{initial}}] = [E_{\text{final}} - E_{\text{initial}}] - [(TS)_{\text{final}} - (TS)_{\text{initial}}] \quad (4)$$

The entropy, S, is multiplied by the temperature T in order to give all the terms the dimensions of energy. The first bracket is made positive and the second negative (we want only the difference, and the difference *could* have been taken in the other order) in order to make the change in free energy for a spontaneous process conform to our prejudice that in a spontaneous process an "energy" should decrease. For a constant temperature process, the temperature symbol can be taken outside the bracket, and

$$[A_{\text{final}} - A_{\text{initial}}] = [E_{\text{final}} - E_{\text{initial}}] - T[S_{\text{final}} - S_{\text{initial}}] \quad (5)$$

or

$$\Delta A = \Delta E - T\Delta S \quad (6)$$

where the Δ symbol is always to be interpreted as representing the expression in the bracket—the difference between the value of the quantity in the final state and the value in the initial state.

For a spontaneous process at constant volume and constant temperature, ΔA is always negative.

$$(\Delta A)_{V,T} < 0 \quad (7)$$

This is in agreement with our previous conclusions for the special cases of constant energy or constant entropy. If the entropy is constant, the sign of the energy change is the decisive factor; ΔS is zero and the system changes to a state of lower energy. E_{final} is less than E_{initial}, ΔE is negative and so, of course, is ΔA. If the energy is constant, ΔE is zero, and the system will go toward the state of higher entropy; hence ΔS is positive, but $-T\Delta S$ is negative and ΔA is negative.

Many chemical reactions are carried out at constant pressure, in vessels exposed to the constant atmospheric pressure, for example. For this situation a different free energy (the Gibbs free energy) has been defined such that, for constant temperature

$$\Delta F = \Delta H - T\Delta S \quad (8)$$

and the criterion of spontaneity is that ΔF shall be negative for a spontaneous process at constant pressure and constant temperature.

$$(\Delta F)_{P,T} < 0 \quad (9)$$

In equation (8) ΔH is the change in enthalpy, measured by the heat of reaction at constant pressure under conditions such that no work is done other than that required to push back the atmosphere.

The condition which tells us that the ball will roll down hill is

$$(\Delta E)_{S,V} < 0 \quad (10)$$

since this process, as most mechanical processes, occurs under conditions of constant entropy and constant volume. Similarly for a system at constant energy and constant volume we have

$$(\Delta S)_{E,V} > 0 \quad (11)$$

The two kinds of free energy each have a physical significance. It can be shown that the change in Helmholtz free energy, ΔA, is equal to the negative of the work done by the system when the process is carried out at constant temperature under conditions such that an infinitesimal change in the conditions will cause the process to reverse itself and proceed in the opposite direction. Such a condition would exist, for example, if a gas were expanding against a piston backed by an external pressure infinitesimally lower than the pressure exerted by the gas itself. A slight increase in the external pressure would then cause the piston to move so as to compress the gas. Under such "reversible" conditions at constant temperature

$$\Delta A = -w_{\text{rev}} \quad (12)$$

The change in the Gibbs free energy, ΔF, represents the work other than work of expansion or contraction against an external pressure done under such reversible conditions. At constant pressure and consta t temperature

$$-\Delta F = w_{\text{rev}} - P\Delta V \quad (13)$$

For this reason, $-\Delta F$ is sometimes called the net work.

Changes in Entropy and Energy in Chemical Reactions

We now have the answer to the title question. You can tell whether a reaction will occur by determining whether the free energy change is negative for the reaction under the specified conditions. The free energy change in turn may be determined if we can determine the change in energy (or enthalpy) and the change in entropy for the process. What generalizations can we make about the sign and magnitude of the two terms?

The enthalpy change for a reaction corresponds to the heat of reaction. This is related most directly to the change in numbers and strengths of bonds as the system changes from reactants to products. In the reaction of water gas formation, for example, the carbon-to-carbon bonds in the coke and the two hydrogen-to-oxygen bonds in each molecule of steam must be broken, while hydrogen-to-hydrogen bonds and bonds between carbon and oxygen of a special sort are formed. We imagine the reaction to go through an intermediate stage of free atoms, as shown in Figure 2. The processes on the left would require 390 kcal; those on the right would liberate 358 kcal. The net effect, as required by the law of conservation of energy, is that 390−358 = 32 kcal must be added. This result is in good agreement with the experimental value, ΔH = +31,400 cal for the reaction at 25°

$$\text{C(graphite)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2\text{(g)} \quad (14)$$

when each gas is at 1 atm.

The enthalpy change in a reaction is not greatly dependent upon the conditions of temperature and pressure. Hence an estimate of this change, which will be nearly correct for any conditions, can always be made by considering the differences in bond strengths.

Since ΔH is positive for the water gas reaction, the free energy change can be negative, for the spontaneous reaction, only if $T\Delta S$ is positive and larger than ΔH. ΔS will be positive if the products are in a more random state than the reactants. The products are gases, but one of the reactants is a solid (a highly ordered state). It is easy to see therefore that the change from the ordered solid state to the random gaseous state must proceed with an increase in entropy, and for the water gas reaction at 25°, when each gas is at 1 atm, the increase amounts to 32.0 calories per degree for the molar quantities of equation (14). It will be generally true that a change from a solid to a gaseous state will proceed with an increase in entropy.

If all the reactants and products are gases, the sign of the entropy change is often determined by the change in the number of molecules. This is related to the possibilities of energy distribution within molecules as developed in the following paragraph.

We have seen earlier, in considering the mixing of helium and neon, that the entropy increases with increase in the number of places to put the molecules; hence, there is an increase in entropy with increase in volume. Molecules, however, may not only be put in different places in space, but also in different "places" in an energy sense. A molecule may hold energy in many different ways, as energy of electronic excitation, of vibrational motion of the atoms in the molecule, as rotational (spinning) motion of the molecule as a whole, or as the kinetic energy of translational motion of the molecule as a whole. Each of these energies is more or less independent of the other, and each of them is quantized. The difference in energy between one quantum level and the next, however, varies markedly among the four kinds. This difference is largest for electronic energies, and decreases in the order listed, being smallest for translational energies. The result is that for electronic and vibrational energies there may be accessible to the molecules only one or a few energy "places," whereas for translational energies there will be many places available to a group of molecules with limited energies. Since there are many more places to put the molecules, energy-wise, in translational motion than there are in the other types of motion, the entropy for the translational motion will be much larger than for the other types.

Consider now the entropy change in a dissociation such as that of nitrogen molecules to nitrogen atoms.

$$N_2(g) \rightarrow 2N(g) \qquad (15)$$

From what has been said above, the electronic terms will make little contribution to the entropy effects. We note, however, that we have two particles in the product, and hence two sources of translational entropy, but only one such source in the reactant. The reactant molecules do have vibrational and rotational entropies. When change occurs in the direction of the arrow there is a loss of the entropy terms due to vibration and rotation, which are not present at all in the nitrogen atoms, and a change from translational entropy for one particle to translational entropy for two. Due to the closeness of quantum level spacing for the translational energies, however, the increase in entropy resulting from the added translational terms in the product more than compensates for the loss of the rotational and vibrational terms in the reactant, and the over-all effect is an increase in entropy. This result is of general application; an increase in the number of particles produces an increase in entropy, so that dissociation processes in gases proceed with an entropy increase. As with the enthalpy, the magnitude of ΔS does not change greatly with change in temperature, unless there is a change in physical state at the melting or boiling point of one of the substances, or a change from one solid phase to another, within the temperature range considered.

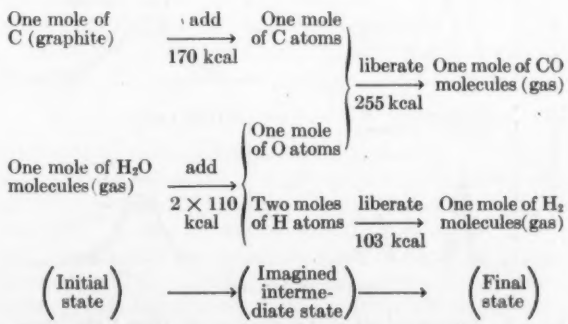

One mole of C (graphite)
add 170 kcal
One mole of C atoms
liberate 255 kcal
One mole of CO molecules (gas)
One mole of O atoms
One mole of H_2O molecules (gas)
add 2×110 kcal
Two moles of H atoms
liberate 103 kcal
One mole of H_2 molecules (gas)
Initial state
Imagined intermediate state
Final state

Figure 2. Hypothetical mechanism for the water-gas reaction.

Since ΔS is positive for dissociation processes, it means that at some temperature all such processes become spontaneous, no matter how much energy the dissociation requires, for at a sufficiently high temperature $T\Delta S$ must always become greater than ΔH, so that the difference $\Delta H - T\Delta S$ becomes negative. Everything dissociates at high enough temperatures.

The last paragraph points out the effect of the temperature term in the free-energy expression. The reaction of water gas formation from graphite at 25°C when each gas is at 1 atm is not spontaneous, since for these conditions

$$\Delta F = +31{,}400 - 298 \times 32.0 = +21{,}900 \text{ calories} \qquad (16)$$

At 1000°, however, we have, if ΔH and ΔS are constant,

$$\Delta F = 31{,}400 - 32{,}000 = -600 \text{ calories} \qquad (17)$$

and the reaction is spontaneous. Thus we see that at low temperatures, the sign of the energy term is the controlling factor. At high temperatures this may be reversed by the entropy term. The statements of Thomsen and Berthelot are correct, therefore, at low enough temperatures, when $T\Delta S$ is small compared to ΔH, and the reaction *does* go in the direction predicted by the energy change. At absolute zero the statements of Thomsen and Berthelot are exact; van't Hoff appears to have been the first to emphasize this.[5]

Bibliography

BERRY, A. J., "From Classical to Modern Chemistry," Cambridge, The University Press, 1954, pp. 33–36.

Memorial Lectures Delivered Before the Chemical Society, Vol. II, London, Gurney and Jackson, 1914: "Thomsen Memorial Lecture," by T. E. THORPE, (1910); and "Berthelot Memorial Lecture," by H. B. DIXON (1911).

GLASSTONE, S., AND LEWIS, D., "Elements of Physical Chemistry," D. Van Nostrand and Co., Inc., Princeton, N. J., 1960, Chaps. 3 and 4.

MOORE, WALTER, "Physical Chemistry," 3rd ed., Longmans Green and Co., 1957, New York, Chaps. 3, 4, and 12.

[5] VAN'T HOFF, J. H., "Etudes de dynamique chimique," Frederick Muller et Cie, Amsterdam, 1884, Part IV, Section 4.

William Rieman III
Rutgers, The State University
New Brunswick, New Jersey

Salting-Out Chromatography

A review

Wheaton and Bauman (*1*) discovered that some water-soluble organic nonelectrolytes (or weak electrolytes) can be separated from each other by elution with water through columns of ion-exchange resins. For example, they separated a mixture of sucrose, glycerol, triethylene glycol, and phenol by this method. The components emerged from the column in the order given.

In the author's laboratory, methanol, ethanol, and propanol-1 were eluted individually through a column of Dowex 1-X8 in the sulfate form with water as eluent (*2*). As indicated by the continuous lines of Figure 1, the graphs overlap so badly that a satisfactory separation cannot be achieved by elution with water. The

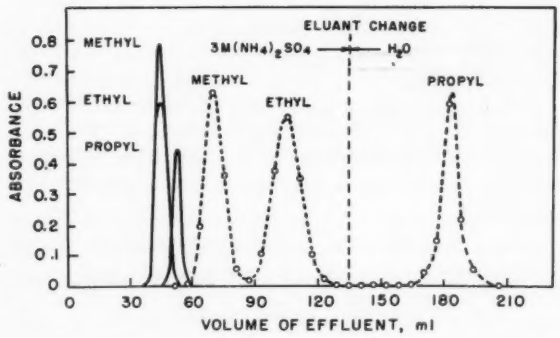


Figure 1. Comparison of the separability of alcohols with water and 3 *M* $(NH_4)_2SO_4$ as eluents. Dowex 1-X8, 200–300 mesh, 25.7 cm × 2.28 cm^2, 0.5 cm/minute. [From *J. Org. Chem.*, 21, 594 (1956).]

ordinate is the absorbance of the Cr(III) formed by the reduction of dichromate by the alcohol and is therefore proportional to the concentration of alcohol in the eluate. The broken lines of this figure indicate the elution graph of a mixture of these three alcohols through a column of the same resin and the same dimensions with 3 *M* ammonium sulfate as eluent. After the elution of the ethanol, the eluent was changed to water to hasten the removal of the propanol-1. Without this change, the peak of the graph of the propanol would have been reached at a volume of 475 ml.

The presence of the salt in the eluent has two effects: (1) It moves each elution curve to the right. This is due to the fact that the salt decreases the solubility of the organic solute in the aqueous phase (or tends to salt it out of aqueous solution), thus increasing its partition coefficient between the resin and aqueous phases. (2) It increases the distance between the individual curves and hence improves the separation. This fortunate fact is due to the great selectivity of the salting-out effect.

The term, *salting-out chromatography*, is applied to the chromatography of organic nonelectrolytes through ion-exchange resins with salt solutions as eluents.

Figure 2 illustrates the effects of some variables on the elution graphs of salting-out chromatography (*3*). Part *A* shows the elution of propylene glycol with 3 *M* ammonium sulfate as eluent through three different anion-exchange resins. All the columns had the same dimensions, and all the resins were in the sulfate form to avoid ion exchange. Dowex 1, a strong-base resin, gives the narrowest graph and hence is the best resin. Dowex 2, with nearly the same basic strength, is almost as good. The weak-base resin, Dowex 3, is much less satisfactory. The same situation prevails among the cation exchangers. The strong-acid resin, Dowex 50 (ammonium form), gives a graph almost identical with that of Dowex 1; and a carboxylic resin in the ammonium form gives a graph very similar to that of Dowex 3.

Part *B* shows the elutions of propylene glycol through columns of Dowex 1-X10 with 3 *M* ammonium sulfate. As is to be expected, the finer particles give the better results.

Part *C* shows elutions of a mixture of methanol and ethanol through columns of Dowex 1 of different degrees of crosslinking with 3 *M* ammonium sulfate as eluent. The best separation was obtained with the resin made from 8% divinylbenzene, *i.e.*, 8% crosslinked. However, with solutes of much larger molecular size, Dowex 1-X4 is sometimes preferable because large molecules have difficulty diffusing into and out of highly crosslinked resins.

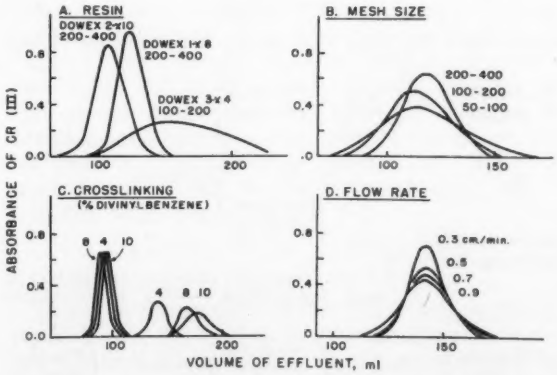


Figure 2. Variables in salting-out chromatography. [From *J. Phys. Chem.*, 61, 354 (1957).]

Based on a paper read as part of the Symposium on Recent Advances in Analytical Chemistry before the Division of Chemical Education at the 138th Meeting of the ACS, New York City, September, 1960.

Part *D* indicates, as is to be expected, that slow flow rates give better elutions. Rates of about 0.5 cm/minute (0.5 ml/cm² minute) are generally satisfactory.

The eluent salt should meet three requirements: large salting-out effect, large solubility, and noninterference in the determination of the separated organic compounds.

Alcohols (*3*), ethers (*4*), aldehydes and ketones (*5*), and some amines (*6*) can be conveniently determined by treatment of an aliquot of the aqueous solution with an equal volume of a solution of sodium dichromate in concentrated sulfuric acid and subsequent spectrophotometric determination of the resultant chromium (III) (*7*). Interfering salts are those that oxidize these organic compounds or reduce dichromate under these conditions. This criterion eliminates all of the common anions except sulfate, acetate, and phosphate. On the other hand, a wide variety of noninterfering cations is available. Ammonium sulfate is a very good eluent salt for most separations.

If the quantity of organic compounds taken for elution is too large, the graphs are wide and subject to tailing (descending slope less than ascending slope); then separation is impaired. In general, the quantity of the most abundant constituent of the sample should not exceed 0.002 mmol for each milliliter of bed volume.

Effect of the Concentration of the Eluent

Each of several alcohols was eluted through a column of Dowex 1-X8 several times, each time with a different concentration of ammonium sulfate as eluent. The value of U^*, the volume of eluate collected from the addition of the sample to the peak of the elution graph, was read from the graph of each elution. Then the corresponding value of C was calculated for each elution from the equation (*8*)

$$C = (U^*/V) - 1$$

C is the distribution ratio, defined as the quantity of sample constituent in the resin phase of any plate of the column divided by the quantity of the same constituent in the interstitial solution of the same plate at equilibrium. V is the interstitial volume of the column. The determination of V has been described elsewhere (*9*).

Figure 3 is a plot of log C *vs* molarity of the eluent for the various alcohols studied. For each alcohol, the points lie on a straight line within the experimental error. Therefore one may write the equation

$$\log C = \log C_0 + kM \qquad (1)$$

C_0 is the distribution ratio with water as eluent; M is the molarity of the ammonium sulfate; and k is a constant characteristic of the alcohol and salt.

Equation (1) is very similar to the Setschenow (*10*) equation

$$\log S = \log S_0 - kM \qquad (2)$$

where S_0 is the solubility of a nonelectrolyte in pure water, S the solubility in a salt solution of molarity M, and k a constant characteristic of the nonelectrolyte and salt. It was of interest to learn if k for any given salt and alcohol has the same value in equation (1) as in equation (2). Table 1 lists the parameters of equation (1) and also k of equation (2) for a few alcohols.

The values of C_0 for any given alcohol differ from resin to resin. They are a measure of the attraction between the resin and the nonelectrolyte. The more hydrophobic compounds have the larger C_0 values. On the other hand, the values of k in equation (1) for any one alcohol are the same for Dowex 1-X8 as for Dowex 50-X8 and also check the k of equation (2). This indicates that k is a salting-out constant and depends only on the nonelectrolyte and the salt.

Table 1. Values of C_0 and k

Alcohol	Dowex 1-X8 log C_0	Dowex 1-X8 k	Dowex 50-X8 log C_0	Dowex 50-X8 k	Eq. (2) k
Methyl	−0.252	0.158	−0.095	0.151	
Ethyl	−0.208	.256	−0.083	.243	
n-Propyl	+0.070	.336	+0.043	.330	0.341
sec-Butyl	.150	.422	.039	.407	.420
n-Butyl	.35	.40	.125	.405	

Resins with crosslinking greater than 8% give the same k values as those with 8% crosslinkage. Resins with less than 8% divinylbenzene, however, give smaller values of k. This is illustrated in Table 2.

Table 2. Effect of Crosslinkage on k

Resin	Acetone	Butanone
Dowex 1-X8	0.318	0.397
Dowex 50-X8	.314	.398
Dowex 1-X4	.283	.360
Dowex 50-X4	.272	.358

All ion-exchange resins undergo a volume change when the concentration of the ambient salt solution is

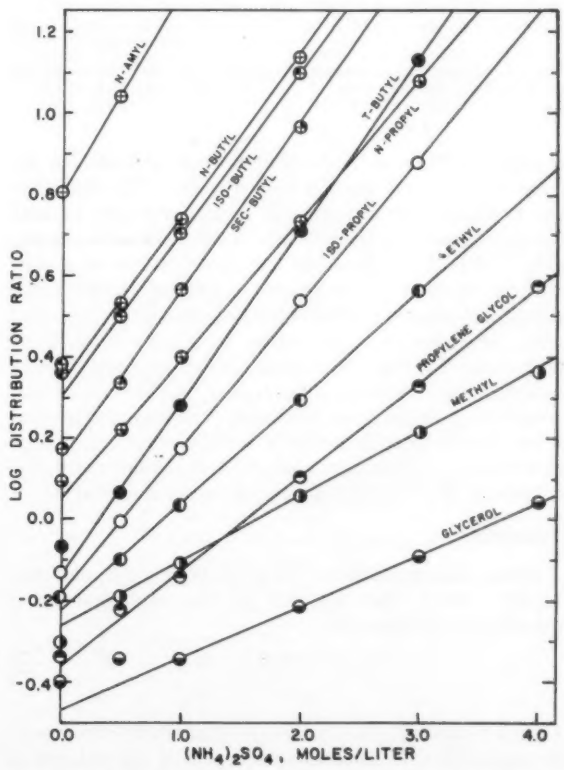


Figure 3. Plots of log C vs concentration of $(NH_4)_2SO_4$ for alcohols with Dowex 1-X8. [From *J. Phys. Chem.*, 61, 354 (1957).]

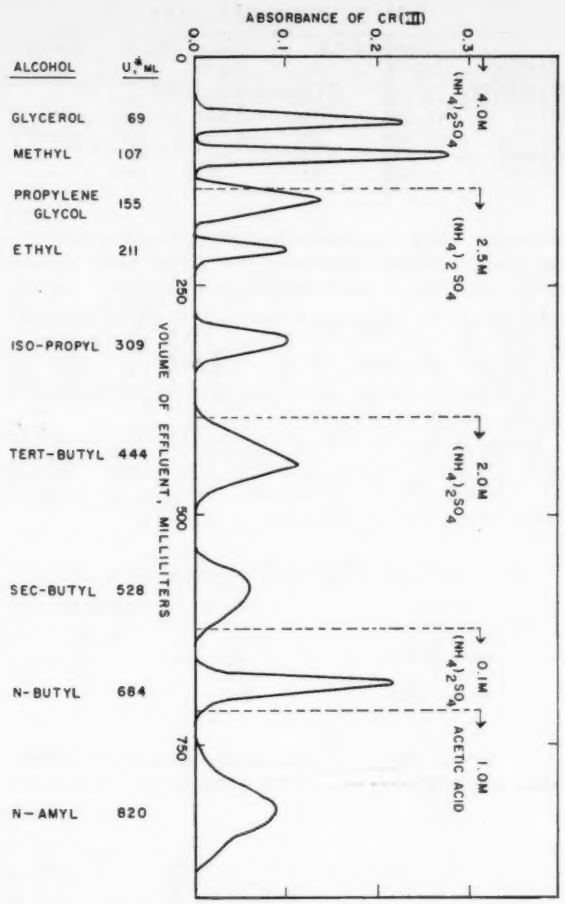


Figure 4. Separation of alcohols with Dowex 1-X8, 200–400 mesh, 32.0 cm × 2.28 cm², 0.6 cm/minute. [From *J. Phys. Chem.*, 61, 354 (1957).]

changed. They shrink when the concentration is increased and swell when it is decreased. The extent of the swelling and shrinking is small for resins of high crosslinkage. Therefore these resins present a reasonably constant environment for the sorption of a nonelectrolyte as the concentration of the external salt solution is altered. Therefore the salting-out constant with these resins is the same as in the Setschenow equation. On the other hand, as the concentration of external salt solution is increased, the resins of low crosslinkage undergo considerable shrinkage and present a less favorable environment for the sorption of nonelectrolytes. Therefore k of any one nonelectrolyte decreases as the crosslinkage of the resins is decreased.

Separations

From the equations of the plate theory (*8*), one may readily derive the equation of the condition for a quantitative separation

$$\frac{C_2}{C_1} = \frac{\sqrt{HP} + 3.29}{\sqrt{HP} - 3.29} \qquad (3)$$

C_2 and C_1 denote the C values of two nonelectrolytes to be separated; H denotes the length of the column in centimeters and P the number of theoretical plates per centimeter. The number 3.29 is taken from a table of probability integrals and corresponds to a separation 99.95% complete. In the derivation of this equation, it was assumed that $C - 1 \cong C$. Therefore the equation is inaccurate for very small values of C_1 and C_2. With the alcohols studied, the values of P varied somewhat but were always close to 9.0. A value of 30 cm was arbitrarily selected for H. By substitution of these values in equation (3), it is found that the condition for the separation of any two alcohols is $C_2/C_1 \geqq 1.50$ or

$$\Delta \log C = \log C_2 - \log C_1 \geqq 0.176 \qquad (4)$$

By application of this equation to Figure 3, it is seen that *n*-butyl and isobutyl alcohols cannot be separated with any concentration of ammonium sulfate, that methanol and glycerol can be separated with any concentration, that propylene glycol and methanol can be separated with 4 M ammonium sulfate but not with smaller concentrations of this salt, etc.

In this manner, a sequence of eluents was selected that should theoretically give a quantitative separation of the nine alcohols shown in Figure 4. A mixture of these alcohols was then eluted through a 32-cm column (7% factor of safety) with the predetermined sequence of eluents. The excellent separation shown in Figure 4 indicates the reliability of the plate theory and equation (3).

Similar studies were made of the chromatographic behavior of ethers (*4*), aldehydes and ketones (*5*), and amines (*6*). Ammonium sulfate was used as the eluent salt with the ethers, aldehydes, and ketones; and linear graphs of log C *vs* M were found. The amines presented a slightly different problem. In order to maintain the amines essentially in the nonionized state, an alkaline eluent was necessary. Tertiary potassium phosphate was selected. As indicated in Figure 5, the plots of log C *vs* M are curved, especially at low values of

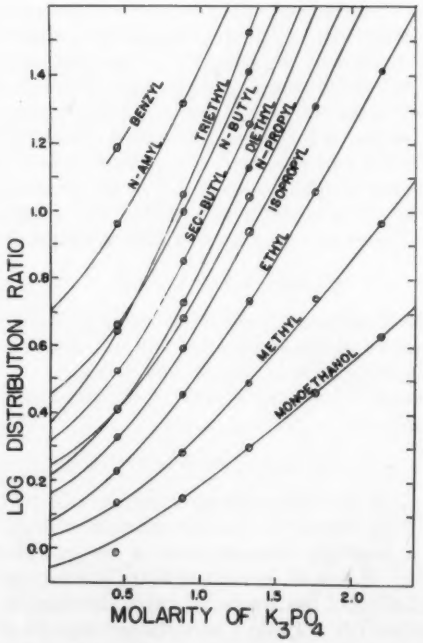


Figure 5. Plots of log C *vs* concentration of K_3PO_4 for amines with Dowex 50-X4. [From *Anal. Chim. Acta*, 17, 408 (1957).]

M. This curvature is due to the hydrolysis of the tertiary phosphate ion and the fact that the ionic salting-out constant of the secondary phosphate ion plus that of the hydroxide ion is not equal to that of the tertiary phosphate ion. Nevertheless, Figure 5 was used to select a sequence of eluents for the separation of eleven amines as indicated in Figure 6. Figures 7, 8, and 9 show respectively the separations of some ethers, aldehydes, and ketones.

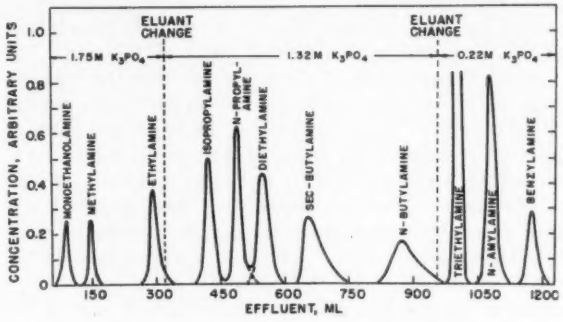


Figure 6. Separation of amines with Dowex 50-X4, 200–400 mesh, 27.5 cm × 2.28 cm², 0.4 cm/minute. [From *Anal. Chim. Acta*, 17, 408 (1957).]

Low-Capacity Resins

Salting-out chromatography is a special case of inverse-phase partition chromatography. The question came to mind whether it was necessary to use ion-exchange resins as the stationary phase. Accordingly, several organic compounds were eluted through columns of crosslinked polystyrene free of ion-exchange groups. Both water and salt solutions were used as eluents. In

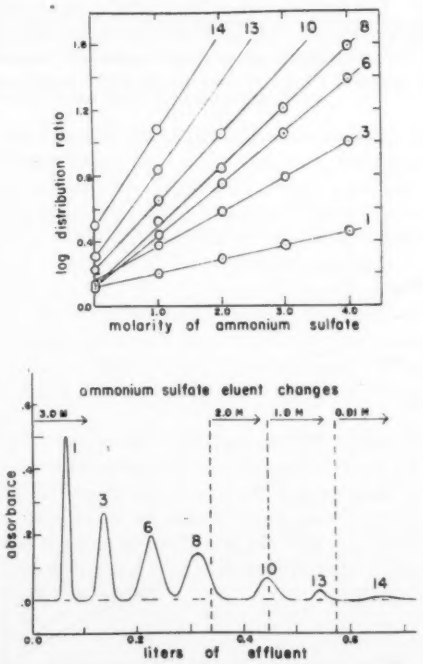


Figure 7. Separation of ethers with Dowex 50-X4, 200–400 mesh, 14.0 cm × 3.90 cm², 0.7 cm/minute. 1 = ethanediol-1,2. 3 = 2-methoxyethanol-1. 6 = 1-methoxypropanol-2. 8 = dimethoxyethane-1,2. 10 = diethyl ether. 13 = di-isopropyl ether. 16 = di-*n*-propyl ether. [From *Anal. Chim. Acta*, 18, 197 (1958).]

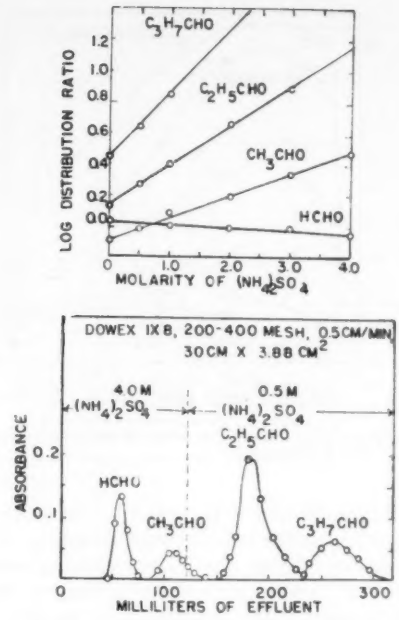


Figure 8. Separation of aldehydes. [From *Anal. Chim. Acta*, 18, 204 (1958).]

all cases, values of C were practically zero, i.e., the peak of the elution graph came at $U^* \cong V$. This aroused curiosity as to how resins would function in salting-out chromatography if they contained some ion-exchange groups but less than the usual Dowex 1 or Dowex 50.

Such resins were not available commercially; but, at the request of the author, The Dow Chemical Company kindly prepared several resins similar to ordinary Dowex 50-X8 and Dowex 1-X8 except that they contained less than the normal amount of the functional

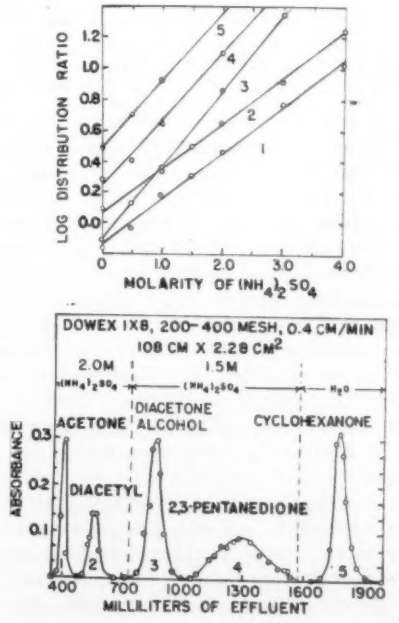


Figure 9. Separation of ketones. [From *Anal. Chim. Acta*, 18, 204 (1958).]

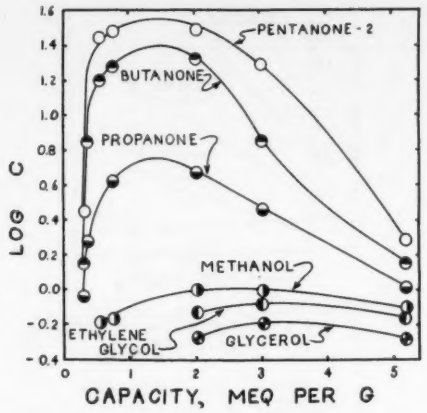


Figure 10. Plots of log C_0 *vs* capacity of sulfonated polystyrenes. [From *J. Phys. Chem.*, **63**, 1511 (1959).]

groups, $-CH_2SO_3H$ and $-CH_2NMe_3Cl$. In other words, these resins had lower ion-exchange capacities than the ordinary resins. Since the cation-exchange resins of this type were investigated more thoroughly than the anion exchangers, this discussion is limited to the former.

Several elutions were performed with each of several organic compounds through each of these low-capacity cation exchangers in the ammonium form. Both water and solutions of ammonium sulfate were used as eluents. From each elution, the value of C was evaluated. Plots of log C *vs* the capacity of the resin were made. Figure 10 shows these plots for six organic compounds with water as the eluent. This figure illustrates the following points: (1) as the capacity is decreased from the normal value of 5.2, the graph rises to a maximum and then falls; (2) the maximum occurs at lower capacities with hydrophobic compounds than with hydrophylic compounds; (3) in general, the vertical distance between any two curves, $\Delta\log C$, increases as the capacity is decreased from 5.2 to about 2.0. This indicates that separations should be more readily accomplished with a low-capacity resin than with a normal resin.

There is another factor, however, which militates against the use of low-capacity resins. They imbibe less water than the normal ion-exchange resins; hence diffusion of solutes inside these resins is slower, and equilibrium between the resin and external phase is established more slowly. Therefore an elution through a low-capacity resin must be done at a smaller flow rate, or tailing and poor separation will ensue. Fortunately, these undesired effects are not serious with resins of capacities of four or greater; and, as indicated in Figure 10, most values of $\Delta\log C$ are markedly improved by decreasing the capacity of the resin from 5.2 to 4.0. Therefore, sulfonated polystyrene resins with capacities of about 4 meq per g are recommended for difficult separations.

Such a resin has been used, for example, in the analysis of mixtures containing orthophosphoric acid, four of its dialkyl esters, and four alkanephosphonic acids (*11*). The alkyl groups were methyl, ethyl, isopropyl and *n*-butyl. Gas chromatography is not applicable to these mixtures because of the nonvolatility of the components. Anion-exchange chromatography was less successful than salting-out chromatography through a cation exchanger of capacity 4.0 meq per g with eluents of lithium chloride and/or hydrochloric acid. The acid served to repress the ionization of the phosphorus acids. A similar method has also been used to analyze 19-component mixtures containing the monoalkyl esters of the alkanephosphonic acids in addition to most of the compounds mentioned above.

The following purely qualitative explanation of the shapes of the curves in Figure 10 is offered. Four phenomena enter into the sorption of an organic compound by ion-exchange resins: (1) Simple dissolution of the compound in the internal water of the resin. (2) Van der Waals forces of attraction between the benzene rings of the resin and the hydrocarbon part of the solute. (3) Attractive forces exerted by the fixed and counter ions of the resin on the dipole of the organic solute. (4) Repulsive forces exerted by the fixed and counter ions of the resin on the nonelectrolyte; these are "salting-out" forces striving to drive the organic compound back into the external phase. The first two are probably the most important. As the capacity of a resin is decreased, the percentage of the hydrocarbon part of the resin is increased; thus the van der Waals forces and hence the sorption are increased. Further decreases in capacity cause a marked decrease in the amount of internal water and hence decrease the sorption.

Solubilization Chromatography

As indicated in Figure 4, the last eluent to be used in the separation of the alcohols was 1.0 M acetic acid. If the elution had been continued with 0.1 M ammonium sulfate or with water, the peak of *n*-amyl alcohol would have been much further to the right and much more time would have been required to complete the elution. The acetic acid in the eluent plays exactly the opposite role as salt. It increases the solubility of amyl alcohol in the aqueous phase, and hence decreases C and U^*. It seemed likely therefore that the application of

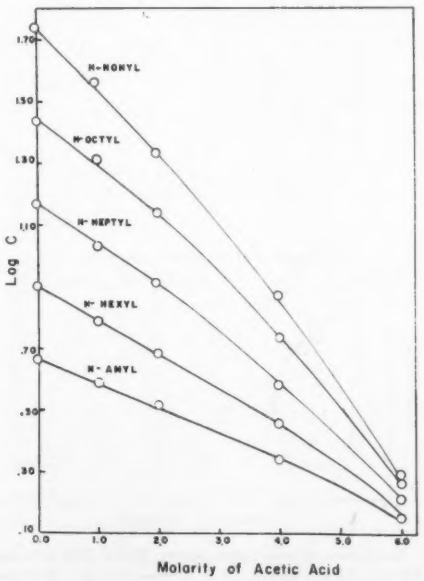


Figure 11. Plots of log C of alcohols *vs* concentration of acetic acid in eluent with Dowex 50-X8. [From *Anal. Chim. Acta*, **18**, 214 (1958).]

ion-exchange resins as the stationary phase in the chromatographic separation of organic nonelectrolytes could be extended to compounds of very small solubility in water by using as eluents aqueous solutions of acetic acid, ethanol, acetone, or similar compounds. This method is called *solubilization chromatography*.

Figure 11 shows a plot of log C of several alcohols *vs* the molarity of the acetic acid. As is to be expected, the slopes are negative. Unfortunately, the graphs are not entirely linear and tend to converge at large concentrations of eluent. This imposes a limit on the molecular size of the alcohols that can be separated by solubilization chromatography. For example, in order to elute decyl alcohol from a column in a reasonable volume, the concentration of acetic acid would have to be 4 or 5 M. At these large concentrations, the values of $\Delta \log C$ are small so that satisfactory separations are impossible. A similar situation exists with other homologous series.

Figures 12, 13, and 14 illustrate respectively the separation of alcohols, ketones, and aromatic hydrocarbons by solubilization chromatography.

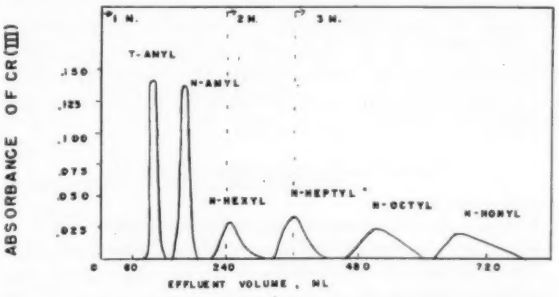


Figure 12. Separation of alcohols by solubilization chromatography with Dowex 50-X8, hydrogen form, 200–400 mesh, 39.0 cm × 2.28 cm², 0.45 cm/minute. [From *Anal. Chim. Acta*, **18**, 214 (1958).]

Comparison with Gas Chromatography

Since both gas chromatography and the methods discussed in this paper deal primarily with the separation of organic compounds, a comparison is inevitable. Gas chromatography has two important advantages: (1) Solubilization chromatography is limited to compounds of about 12 or fewer carbon atoms, whereas gas chromatography is applicable to almost any compound that can be volatilized without decomposition. (2) Gas chromatography is much faster. The elution times for the separations illustrated in the figures of this paper range from 3.0 hours for Figure 8 to 24 hours for Figure 13.

On the other hand, salting-out and solubilization chromatographies also have some advantages: (1) The apparatus is much simpler and less expensive. (2) They are applicable to certain nonvolatile compounds such as the organic acids of phosphorus. (3) They are particularly well suited for samples that are received as dilute aqueous solutions.

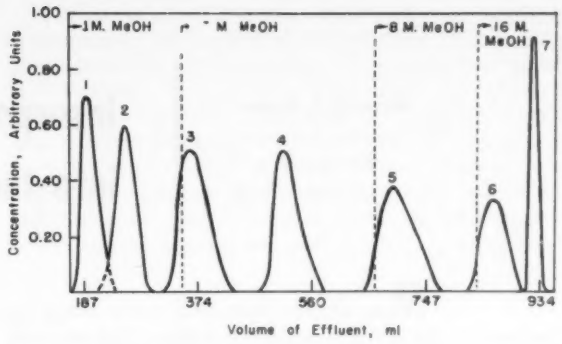


Figure 13. Separation of ketones by solubilization chromatography with Dowex 50-X8, hydrogen form, 200–400 mesh, 54.5 cm × 2.28 cm², 0.28 cm/minute. 1 = 4-methylpentanone-2. 2 = hexanone-2. 3 = heptanone-2. 4 = octanone-2. 5 = nonanone-2. 6 = decanone-2. 7 = undecanone-2. [From *Anal. Chim. Acta*, **19**, 134 (1958).]

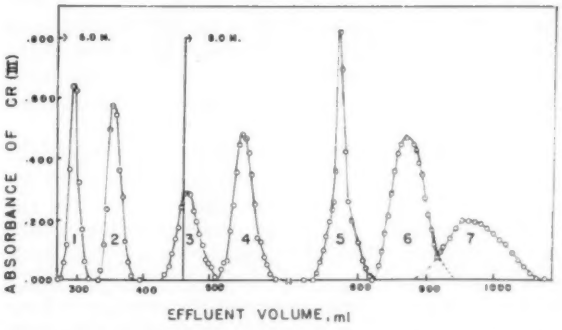


Figure 14. Separation of aromatic hydrocarbons by solubilization chromatography with Dowex 1-X4, acetate form, 200–400 mesh, 60.0 cm × 2.28 cm², 0.28 cm/minute, acetic acid as eluent. 1 = benzene. 2 = toluene. 3 = *m*-xylene. 4 = mesitylene. 5 = naphthalene. 6 = β-methylnaphthalene. 7 = 1,4-dimethylnaphthalene. [From *Anal. Chim. Acta*, **20**, 357 (1959).]

Literature Cited

(1) Wheaton, R. M., and Bauman, W. C., *Ann. N. Y. Acad. Sci.*, **57**, 159 (1953).
(2) Sargent, R., and Rieman, W., *J. Org. Chem.*, **21**, 594 (1956).
(3) Sargent, R., and Rieman, W., *J. Phys. Chem.*, **61**, 354 (1957).
(4) Sargent, R., and Rieman, W., *Anal. Chim. Acta*, **18**, 197 (1958).
(5) Breyer, A., and Rieman, W., *Anal. Chim. Acta*, **18**, 204 (1958).
(6) Sargent, R., and Rieman, W., *Anal. Chim. Acta*, **17**, 408 (1957).
(7) Sargent, R., and Rieman, W., *Anal. Chim. Acta*, **14**, 381 (1956).
(8) Rieman, W., and Sargent, R., "Ion Exchange" *in* "Physical Methods of Chemical Analysis," edited by W. G. Berl, Volume 4, Academic Press, New York, in press.
(9) Manalo, G. D., Turse, R., and Rieman, W., *Anal. Chim. Acta*, **21**, 383 (1959).
(10) Setschenow, J., *Z. physik. Chem.*, **4**, 117 (1889).
(11) Jakob, F., Park, K. C., Ciric, J., and Rieman, W., *Talanta*, in press.

Norman S. Radin[1]
Northwestern University
Medical School
Chicago, Illinois

Incorporating Radioisotope Techniques into the Chemistry Curriculum

Most efforts that have been made by teachers of chemistry to acquaint college students with the value of radioisotopes have emphasized the radiochemical and physical aspects of these isotopes. This point can be seen by perusing the collection (*1*) of papers published in THIS JOURNAL on radioisotopes. The topics of decay, parent-daughter relationships, nuclear activation, and nuclear chemistry have been frequently applied to teaching experiments. Where the more chemical uses, such as isotopic dilution and radiometric analysis, have been described, most of the experiments have taught simply another aspect of radioactivity rather than a fundamental chemical principle or fact.

This emphasis is neglectful of many other important applications of radioactivity and there is a need for experiments which bring these applications into the ordinary chemical curriculum. Such experiments cannot be designed as "extra" experiments, for there is no extra time in the student's or teacher's day. If the teacher is to substitute a radioactivity experiment for a presently accepted experiment, he must sacrifice the illustration of an important chemical topic. If, as in so many schools, the applications of radioactivity are taught in a special, advanced course, only a few students will become familiar with these new principles and they will have to give up time that might be better spent in studying their main field of chemistry.

The problem posed can be solved by developing experiments which include realistic radioisotope uses, but only as a secondary feature. The experiments must teach the important chemical subject matter, so that chemistry teachers can freely displace one or more standard experiments. For optimum realism and acceptability, the new experiments should be available in all levels of college chemistry.

The principles of design cited above have been the basis for a new laboratory manual (*2*), which was cosponsored by the U. S. Atomic Energy Commission and Nuclear-Chicago Corporation, and prepared by the writer and a group of other teachers. An outline of the chemistry experiments in this manual is shown in the table.

It can be seen that in many experiments the isotopic technique has simply replaced the more usual gravimetric, volumetric, or colorimetric techniques of analysis. Such an exchange will surely not cause any serious weakening of the student's training in these standard procedures, for the student receives multiple exposure to these methods anyway. In the organic chemistry experiments, standard synthetic reactions have simply been modified to allow use of isotopic starting materials. In some of the experiments, the peculiar properties of tracers allow us to demonstrate chemical principles that could not be demonstrated otherwise; however, such demonstrations need not lack for other important chemical reactions or properties.

Typical Radioisotope Experiments (2)

Introductory Chemistry:
- Determination of atomic weights, with S^{35}-sulfate.
- Chemistry of sulfur; thiosulfate, sulfur, and sulfite.
- Secular equilibrium; Pb^{210}-Bi^{210}.

Qualitative Analysis:
- Determination of a solubility product for calcium sulfate.
- Separation of ions by liquid/liquid extraction.
- Coprecipitation phenomena; calcium and permanganate with barium sulfate.

Quantitative Analysis:
- Determination of phosphate in a phosphate rock by an isotopic yield method.
- Determination of the formation constant of a complex ion; calcium citrate *vs* an ion exchange resin.
- Determination of calcium; removal of interference by ion exchange and chelatometric titration.

Organic Chemistry:
- Synthesis of S^{35}-sulfanilamide.
- Synthesis of C^{14}-acetylsalicyclic acid.
- Identification of amines by acetylation with C^{14}-acetic anhydride.

Physical Chemistry:
- Dynamic nature of equilibria between ions in solution and a salt.
- Exchange between a metal and ions in solution.
- Analysis of the phase diagram of a three component system; dimethylaniline, water, acetic acid-C^{14}.
- Demonstration of the adsorption isotherm with charcoal and acetic acid.
- Radioactive decay and growth; Ce^{144}-Pr^{144}.

Instrumental Analysis:
- Preparation of samples for Geiger counting.
- Properties of Geiger counters.
- Statistical variation in radioactivity measurements.

Biochemistry:
- Ion exchange and paper chromatography; separation of C^{14}-glycine and glutamic acid; isotopic dilution determination.
- Properties of enzymes, studied with an isotopic substrate made by the student.
- Incorporation of C^{14}-glycine into a protein fraction of mouse spleen; properties of the *in vitro* system.

[1] Present address: Mental Health Research Institute, University of Michigan, Ann Arbor, Michigan.

Sample copies of "Radioisotope Experiments for the Chemistry Curriculum" are available to college and university teachers at no charge on request to Nuclear-Chicago Corporation, 333 East Howard Avenue, Des Plaines, Illinois. Multiple copies for student use may be purchased through Nuclear-Chicago or through the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. at $2 per copy for the experiment manual and $1 per copy for the instructor notes.

Some of the readers may wish to see other topics in chemistry modified to include an isotopic approach, and might be willing to develop such experiments. The purpose of this paper is to describe the practical approaches and principles utilized in the manual in the hope that they will be useful to those interested in preparing their own isotope experiments. It is hoped also that some readers will be encouraged to try introducing such experiments into their own regular chemistry courses.

Counting Systems

Most teachers of chemistry do not have the interest or time to build their own radioactivity instrumentation, and it is fortunate indeed that the Atomic Energy Commission is making available funds to qualified colleges for the purpose of buying good counting equipment and associated supplies. It is now possible for the interested chemistry teacher to plan experiments around the use of accurate, reliable, standard scalers with sensitive thin-window Geiger tubes. High standards of quantitative performance, rather than rough qualitative work, can now be produced by students who work carefully.

The use of standard Geiger tubes of the thin, end-window type means that the radioactive samples (in most cases) must be spread out evenly on planchets. This general procedure gives a reasonable observed activity with a minimum of investment in radioisotopes.

Simplicity of Sample Preparation

The preparation of samples for counting with weak *beta* emitters (the preferred type of isotope for student use) is a topic which deserves very careful attention. Variations in sample preparation are usually the major source of error in radioactivity work and the time required for many procedures of preparation is too great for teaching applications.

The methods that seem simplest—evaporating a small volume of solution, or spreading a slurry of solids—are actually useful only for very small samples (measured with a micropipet) or strong *beta* emitters, such as P^{32}. The most generally useful method, where high precision is wanted, consists of filtering suspended radioactive particles onto a porous planchet. Of the various porous filtering materials that are used in this way, stainless steel discs[2] seem to the writer to be the simplest to use. The steel discs filter rapidly, cannot be broken (unlike sintered glass discs), and are so rigid that they need not be mounted on a backing planchet (unlike paper or Millipore discs). Thus the steel discs are the easiest and fastest to handle and are desirable not only for the inexperienced student but for the research worker. The main drawbacks to the use of steel discs are the high initial expense, the danger of internal radioactivity contamination, and the danger of corrosion. The contamination problem is minimized by the use of a precoat of diatomaceous filter aid, which keeps the radioactive solids from touching the metal surface. The corrosion problem is minimized by careful attention to the properties of stainless steel; the main limitation is lack of resistance to hydrochloric acid.

[2] Micro Metallic Division, Pall Corp., Glen Cove, New York. Porosity G, 1/16" thick.

Holders for steel filter discs have not been available commercially and no serious consideration of these discs has appeared in the literature. It was therefore necessary to design a suitable filtering apparatus, which is sketched in Figure 1. The apparatus consists simply of a Büchner funnel which comes apart. The porous steel disc rests on the lower half of the funnel and the upper half (chimney) screws onto the lower half, holding the disc in place. To make the assembly leak-proof, two Neoprene washers are needed. The upper washer

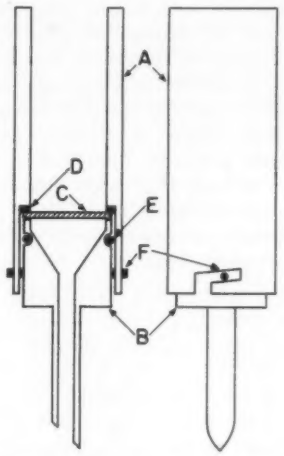


Figure 1. Filter adapter for filtration plating of radioactive suspensions. *A*, upper part (chimney); *B*, lower part; *C*, sintered steel disc; *D*, washer-shaped Neoprene gasket; *E*, O-ring, synthetic rubber; *F*, two steel rods jammed into part *B*. The rods act as screw threads when the chimney is twisted; they tighten down on gasket *D*.

is flat and fits tightly into the chimney so that it doesn't fall out on disassembly. It presses down on the upper face of the steel disc and limits the edges of the radioactive deposit, thereby producing a clean rim to allow handling. The lower washer is an O-ring and is needed to improve the suction and prevent leakage of filtrate when the suction is off. Such a filtering assembly can be made in the school shop out of stainless steel. Approximately 6 students can be served by one assembly, as the filtration step is quite fast. Fortunately, a similar filtering assembly is about to be offered commercially.[3]

To prepare a radioactive sample, one must first add a suspension of diatomaceous earth (Celite Analytical Filter Aid)[4] to the filter assembly and filter off the suspending liquid. The smooth precoat not only prevents contamination but also produces a smoother radioactive deposit. Next the suspension of radioactive material is added and its liquid phase is filtered off. This deposit must be washed with rinse liquid without resuspending the particles, in most cases. After the rinse liquid is pulled through, the filter is disassembled and the steel disc is removed, dried, and counted.

Given this simple technique, one must consider the types of radioactive materials that can be counted. Ion exchange resins, in small mesh size and high cross-linkage, yield uniform but fragile deposits. They can be used to take up ionic radioactive compounds, even from a dilute solution. Adsorbents should be useful

[3] Nuclear-Chicago Corp., Des Plaines, Illinois.

[4] Johns-Manville.

similarly. Many water-soluble radioactive substances can be precipitated with a water-miscible organic solvent, such as alcohol. Conversely, lipoidal substances can be precipitated out with water. Proteins can be precipitated with trichloracetic acid or alcohol. Polyvalent cations can be precipitated by appropriate anions, and *vice versa*. Even neutral substances may be precipitable with a complexing agent, such as urea or picric acid. It is a rare substance that cannot be converted into a suspension suitable for filtration on the steel disc.

Two problems arise in choosing a method for preparing a radioactive suspension: (a) completeness of precipitation, and (b) production of a uniform, stable filter deposit. The first problem, when it arises, can often be evaded by deliberately adding a known amount of non-radioactive carrier, thereby bringing the total weight of deposit above a certain minimum. This minimum, which produces filter cakes that are "infinitely thick," is such that additional yield does not change the observed activity. Thus, variations in yield of precipitate or losses due to washing will not affect the observed activity.

The second problem can be a nuisance and may call for some experimentation. For example, we found that lead hydroxide gives uniform deposits, but bismuth hydroxide yields deposits which curl and crack on drying. Using oxalate as the bismuth precipitant gave us a satisfactory filter cake. The choice of rinse solvent can be important in preventing curling. These and other considerations are discussed elsewhere (*3*).

Close attention should be paid to the appearance of the final radioactive deposits. If the isotope used is a weak emitter (C^{14}, S^{35}, Ca^{45}) and the sample is not infinitely thick, any visible unevenness will yield a grossly inaccurate answer.

Simplicity of Calculations

Another approach that seems useful is the elimination of many of the "technical" complications so common in radioisotope work: corrections for decay, self-absorption, and coincidence losses. These corrections always decrease the precision of counting and are not always essential nor are they intrinsic to most chemical applications of radioisotopes. The problem of decay can be eliminated simply by having each student count a standard with his unknown, both samples being made up similarly from the same isotopic starting material. The coincidence correction appears only with samples showing activities over 4,000 cpm; activities higher than this are not necessary, are wasteful of radioactive materials, and tend to make laboratory contamination a greater danger.

The problem of correcting for self-absorption can be solved by making all samples the same weight or infinitely thick. The former approach is rather restrictive and difficult to arrange except in a few experiments. The latter approach is usually easy to arrange and suffers primarily from the tendency to yield lower observed activities (due to radiation absorption by the extra carrier that may have to be added). Not only does use of infinitely thick samples eliminate correction curves, but it also makes unnecessary the weighing of the planchets and samples, and tends to give more accurate counting, since small irregularities in sample uniformity have little effect.

The mathematics of calculating results from data with infinitely thick samples is not generally known. In the case of infinitely *thin* samples (samples so small that self-absorption is negligible) the observed activity is proportional to the *weight* of the labeled element or compound. However, in the case of infinitely *thick* samples, the activity is proportional to the *concentration* of the labeled element or compound in the sample: $A = kC$. The latter point was illustrated in one of our experiments, in which the atomic weights of various metallic elements are determined by forming insoluble sulfate salts, starting with $Na_2S^{35}O_4$. A portion of the student's sodium sulfate is precipitated from water with methanol, an infinitely thick sample is prepared on a steel filter planchet, and the activity is measured. Given the atomic weights of the elements in this salt, the student calculates the concentration of sulfur (22.5 %) and then the proportionality constant for his counting equipment. Thus, if the sodium sulfate standard shows an activity of 2,250 counts/min (cpm), the constant is $2{,}250/22.5 = 100$. If a heavy metal sulfate (formed from another portion of the sodium sulfate) shows an activity of 1,500 cpm, the sulfur concentration must be $1{,}500/100 = 15.0\%$. From this figure and information about the valence of the metal, the student can readily calculate the atomic weight of the metal.

This method of analysis does contain a weakness, since the backscattering coefficients vary slightly with the average atomic number. Thus, comparison of lead sulfate with sodium sulfate gives an expectedly high activity due to the greater reflection of *beta* rays from the upper portion of the deposit. However, the effect is small and can be explained qualitatively to the students when the experimental results are analyzed.

When the experiment must yield information about a weight, rather than a concentration, the infinite thickness method of sample preparation requires that carrier be added both to the standard and to the unknown. This application is illustrated in an experiment which demonstrates the Freundlich equation for the physical chemistry student. The usual adsorption of acetic acid (radioactive) on charcoal is followed by determining the amount of acetic acid left unadsorbed. To measure the amount of acetic acid, we deliberately dilute it with unlabeled acetic acid, precipitate the silver salt, and filter and count this. A standard, known portion of C-14 acetic acid is processed similarly, and the calculations are something like this:

Standard:

0.4 millimole of C^{14}-acetic acid + 1.2 millimoles of ordinary acetic acid yield an observed activity of 2,000 cpm. The concentration of labeled acid in the mixture is $0.4/(0.4 + 1.2)$ and the basic equation is $A = kC$, so $2{,}000 = k[0.4/(0.4 + 1.2)]$ and $k = 8{,}000$.

Unknown:

x millimoles of labeled acetic acid + 1.2 millimoles of ordinary acid yield an activity of 1,000 cpm. Then $1{,}000 = k[x/(x + 1.2)]$. The student knows k is 8,000 and simply solves for x (0.17 millimole).

Use of Small Amounts of Activity

It is difficult to determine from most published teaching experiments with radioisotopes just how much radioactivity is actually needed. In our experience, the amounts are ordinarily so high that the teacher must

get special authorization from the Atomic Energy Commission in order to obtain the isotopes. This is a serious limitation, and it becomes necessary as a result to design experiments which do not waste radioactivity. Fortunately, it is possible to purchase reasonable amounts of certain radioisotopes without special authorization from the Federal Government, these quantities being the so-called "generally-licensed" amounts. Any teacher can purchase a single package of a generally-licensed amount in the same way that he can purchase any other chemical reagent. Ten such packages may be in one's possession at any moment. The actual quantity of radioactivity in a package depends on the isotope; the figures range from 0.1 microcurie (Sr^{90}) to 50 microcuries (C^{14}, S^{35}). (250 microcuries of tritium can be bought, but this cannot be counted effectively by student-grade equipment.)

In most research experiments involving radioisotopes, the procedure involves counting only a very small fraction of the total amount of activity used, perhaps 0.1% or less. The size of the generally-licensed package does not permit such wastage. Consider the following calculations in this respect. If one has a single generally-licensed package of C^{14}, you have 50 microcuries or $50 \times 2{,}200{,}000 = 110{,}000{,}000$ dpm (disintegrations/minute) which are to be allocated to (say) 30 students. Each student therefore gets 3,700,000 dpm, which is to be divided up, perhaps, between 3 samples. Then each sample will contain 1,200,000 dpm. If this were counted as a very thin sample with a thin-window Geiger counter (efficiency roughly 4%), it would give an observed activity of 48,000 cpm per sample. Under these conditions, one could accept an experiment where 97% of the activity is wasted. If instead the samples are diluted to the point where they weigh 150 mg and therefore give infinitely thick samples on the typical planchet, the efficiency will be somewhat lower (about 1/10) and the observed activity would be about 4,800 cpm. With such a system, we would not like to throw away much more than 80% of the starting activity.

The amount of activity that should be counted by the student depends on the precision desired and the time available for counting. The standard deviation of a measurement is equal to the square root of the number of counts collected, so that a sample counted until 10,000 counts are recorded will have an intrinsic statistical variability of 100 counts, or 1% standard deviation. This is generally considered good precision, especially as the variability in sample preparation may be greater than this. However, the time needed to accumulate such a large number will depend on the actual activity. Thus, a sample exhibiting 10,000 cpm will require only one minute of counting; if the activity is 1,000 cpm, 10 minutes will be needed; if the activity is 100 cpm, 100 minutes will be needed. It is evident that the counting step can be a bottle-neck in a large class when good precision is desired. If possible, the counter should be left running for several days and the students allowed to count in their spare time. To reduce the variability arising from subtraction of the counter's background, this figure should be determined with a long count by the instructor.

The experiment on atomic weight determination described above is ideal with respect to economy of activity as there is virtually no waste at all. One generally-licensed package should suffice for roughly 150 students. In the adsorption experiment described above, the weights of acetic acid and charcoal are chosen so that a reasonable fraction of the acetic acid is left unadsorbed and available for counting.

When one uses an experiment requiring small amounts of activity, one not only avoids the need to get a personal authorization but also greatly reduces the problems of safety and contamination of the laboratory. It must be recognized that no one, including the inexperienced student, is able to work without a certain number of spills in his life. It is therefore to be expected that a certain amount of radioactivity will end up on the floor, table, clothing, or Geiger counter. Obviously, the less activity given to each student, the less serious are the spills. Generally-licensed amounts of activity are ordinarily considered non-toxic even if the student should swallow the entire portion.

It should be pointed out that naturally-occurring radioisotopes can be bought readily in astonishingly high amounts of activity without any question of governmental authorization. Several companies sell an equilibrium mixture of lead, bismuth, and polonium nitrates, all radioactive (atomic weight 210). Only the bismuth radiations are readily detected by a Geiger counter but nearly all the metal atoms in this mixture are lead.

P^{32}, despite its uncomfortably short half-life, makes a good isotope for student work. A generally-licensed package contains only 10 microcuries, but the beta radiation is so penetrating that it is easy to prepare infinitely thin samples even though the weight of the samples is appreciable. 0.06 microcurie in a thin sample will give an ample reading. It is necessary to synchronize your experiment with the delivery schedule of your supplier, as the half-life is two weeks.

Safety Precautions

In ordinary chemical work there is ordinarily a certain amount of spillage or drippage which is considered acceptable. In work with radioactivity, even with student-size portions, it is wise to aim at strictly quantitative procedures with a minimum of handling and contact. Radioactive starting materials should be pipetted out in solution form rather than weighed out by the students, partly because pipetting is normally faster, but mainly because there is less tendency toward spillage. We modified the sulfur-sulfite experiment of McCool and Hentz (*4*) in this way. Where they have the students weigh out powdered S^{35}, we dispense a solution in carbon disulfide into the reaction flask and have each student precipitate his sulfur with acetone. After washing the sulfur with acetone and water, the student heats it with sodium sulfite. In this modification the student also learns something extra about the solubility properties of sulfur as well as the usefulness of Pasteur pipets for handling small volumes of liquid. (Pasteur pipets are simply elongated eye-droppers.)

If possible, solutions should not be poured, even with the aid of pouring rods. There is too much risk of getting radioactivity on the outside of the vessel. It is better to transfer the liquid—if the volume is not too great—with a Pasteur pipet. The transfer can be made complete, if desired, with only a modest volume of rinse liquid, using the same pipet for the rinsing and transferring. Suspensions can also be transferred efficiently

this way, possibly with the aid of a nonionic detergent. We use Pasteur pipets for transferring radioactive slurries to the steel disc filtering device, then for rinsing the inner wall of the chimney and the filter cake on the disc.

In order to avoid pouring, we also try to avoid volumetric flasks and graduated cylinders, substituting pipets where possible. Volumetric flasks are admittedly more accurate than pipets, but often unnecessarily so.

Pipets should not be operated by mouth vacuum, of course. A safety pipettor of some sort should always be used, even when the student pipets a non-radioactive solution (since the pipet top or his fingers may be contaminated). Commercially available safety pipettors work well, but are expensive and a bit of a nuisance to clean if the student should suck radioactive material into the pipettor. We prefer the extremely cheap and simple device described by Kolb (*5*), which we use routinely for pipetting organic solvents and other reagents also. Rodkey's pipettor, readily made from commercially available T-tubes, might be preferred (*6*). With any type of pipettor, it is imperative that the students be given an opportunity to practice its use (with water) during a prior lab period. Pipettors are very easy to use, but practice cannot be avoided.

Incidentally, it should be pointed out that pipets cannot be washed adequately by individual students. We strongly recommend having a student assistant collect the pipets, wash them in a commercial soaker-rinser, and dry them in an oven. This little "luxury" is a great help in maintaining a high level of accuracy in isotopic work. It would indeed be a shame after all this effort and expense to give the students the false impression that radioisotopic techniques lead to inaccurate results.

Literature Cited

(1) A collection of papers from the JOURNAL OF CHEMICAL EDUCATION related to training and experiments in radioactivity, presented by Nuclear-Chicago Corp., 333 East Howard Avenue, Des Plaines, Illinois.

(2) RADIN, NORMAN S., Editor, "Radioisotope Experiments for the Chemistry Curriculum," Nuclear-Chicago Corp., Des Plaines, Illinois, 1960.

(3) Technical Bulletin No. 10, available gratis from Nuclear-Chicago Corp.

(4) MCCOOL, W. J. AND HENTZ, R. R., J. CHEM. EDUC., **32**, 329 (1955).

(5) KOLB, J. J., *Chemist-Analyst*, **47**, 19 (1958).

(6) RODKEY, F. L., *Science*, **118**, 488 (1953).

J. F. Mucci, Dorothy E. Spiegel and **Robert L. Stearns**
Vassar College
Poughkeepsie, New York

Ion Exchange-Radiochemical Experiment

This ion exchange experiment serves the dual purpose of introducing the undergraduate to the concept of the total exchange capacity of a column while giving him an opportunity to use radioisotopes in a quantitative analysis.

A small column (10 cm long and 1.2 cm i.d.) containing the styrene type, sulfonic acid cation exchange resin Dowex 50-X2 (50–100 mesh) is put in the H^+ form by use of a 1 *M* HCl solution. The column is then washed clean of excess H^+ and Cl^- with distilled water. The influents are introduced into the column by siphon action and the rate of flow is regulated with a Hoffman clamp (see Fig. 1). The column is not allowed to go dry during the entire experiment.

A 0.060 *M* aqueous solution of CsCl, spiked with a trace amount of Cs^{137} (half-life 30 years) is allowed to run through the column at the rate of 1 ml/3 min. Fractions of the effluent are collected in previously weighed and dried test tubes by use of a sample collector (Model 1205, Automatic Fraction Collector, Research Specialties Co., Richmond, California). The volume of each fraction is determined by weighing and assuming that the density of the effluent is 1.00 g/ml.

A 6-ml aliquot of each sample is then pipetted into the receiving cup of a dip counter (Radiation Counter Laboratories, Inc., Model 10301). The geometry of the counting system is kept constant by housing the receiving cup and counter in a machined metal holder. A Baird-Atomic Model 123 G.M. Scaler is used for the

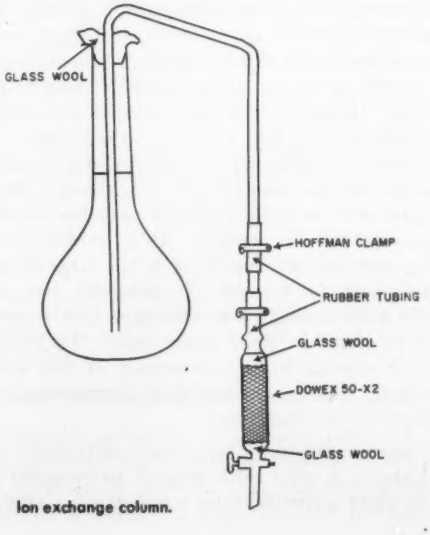


Figure 1. Ion exchange column.

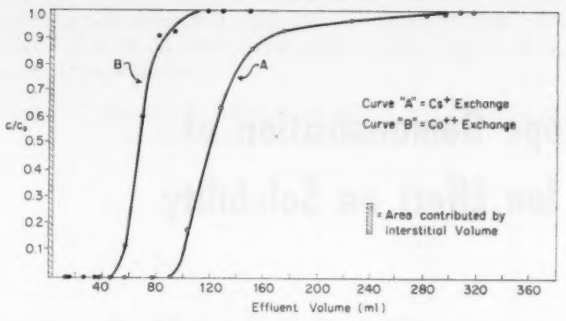


Figure 2. Plot of c/c_0 versus volume for Cs^+ and Co^{+2} exchange on Dowex 50-X2 in H^+-form.

counting measurements and a 2-in. thickness of lead is used to shield the counter.

If c is the number of counts per second from each sample of effluent and c_0 is the number of counts per second from the influent, a plot of c/c_0 versus the effluent volume (mid-point of each sample) can be made as shown in Figure 2-A; c and c_0 are, of course, directly proportional to the molar concentrations of the effluent and influent, respectively. The area above the curve in the c/c_0 versus volume plot determines the total exchange capacity of the ion exchange column (number of meq per column). Although there are more efficient methods[1,2] for determining the total exchange capacity, we have used this one because it fulfills in a simple way the dual purpose of the experiment as stated above.[3]

The column is again put in the H^+ form by allowing 1 M HCl to flow through the column displacing the Cs^+. The excess H^+ and Cl^- are again washed off with distilled water.

At this point a 0.060 M aqueous $CoCl_2$ solution, spiked with a trace of Co^{60} (half-life 5.3 years), is allowed to flow through the column and samples of the effluent are collected as in the case of Cs^+. A plot of c/c_0 versus effluent volume for the Co^{+2} exchange is shown in Figure 2-B.

The trace amounts of radioactive cesium and cobalt were determined by adjusting the counting rates c_0 to give about 100 counts per second. Small counting rate corrections for background and resolving time were made when appropriate.

It should be noted that in both runs the column initially contained water as well as the resin. The volume of the water remaining in the column is known as the interstitial or "hold up" volume. This "hold up" volume has been determined for Dowex 50-X2 and is 30.4% of the bed volume.[4] The area above the curve in the c/c_0 versus effluent volume plot which is contributed by this interstitial volume must of course be subtracted from the total area in determining the total exchange capacity.

The total exchange capacity of the column is a measure of the number of available exchange sites in the resin. This means that, for instance, an ion with a +2 charge can satisfy two exchange sites while it takes two ions of charge +1 to satisfy the same number of sites.

In the runs just described, the molar concentrations of the two influent solutions were the same and therefore the area above the c/c_0 versus volume plot for Cs^+ exchange should be just twice that for the Co^{++} exchange since the total exchange capacity of the column is constant. The ratio of the areas shown in Figure 2 was found to be 1.97. The ratio of the areas above the curves for solutions of the same molarity will only give us the relative charge carried by the exchanging ions when only one ion in known concentration is in solution. For example, some ions such as Al^{+3}, VO_2^+, Th^{+4}, ZnO^{+2}, and Fe^{+3} are only stable in appreciable H^+ concentration and therefore the area above the curve would not be a measure of the charge carried by the ion under investigation.

The authors wish to express their appreciation for financial aid received through an Undergraduate Research Training Program Grant awarded by the National Science Foundation.

[1] "Dowex : : ION Exchange," Dow Chemical Co., Midland, Michigan, 1958, p. 30f.

[2] KUNIN, ROBERT, "Ion Exchange Resins," John Wiley & Sons, Inc., New York, 2nd ed., 1958, p. 340 f.

[3] General references for this type of experimental measurement are to be found in such texts as MEITES, L., AND THOMAS, H. C., "Advanced Analytical Chemistry," McGraw-Hill Book Co., Inc., New York, 1958; and CHASE, GRAFTON D., "Principles of Radioisotope Methodology," Burgess Publishing Co., Minneapolis, Minn., 1959.

[4] MANALO, G. D., TURSE, R., AND RIEMAN, WM., III, *Anal. Chim. Acta*, **21**, 383 (1959).

More Volumes in Nuclear Science Series

The AEC-sponsored series, Radiochemistry of the Elements, now numbers 31 volumes, NAS-NS 3001–3031. [See THIS JOURNAL **37**, 386 (1960) and **38**, 72 (1961).] Each is a monograph containing a general review of the pertinent chemistry and compiles the latest (1960) radiochemical information. All are available from the Office of Technical Services, Dept. of Commerce, Washington 25, D. C.

3015 Zinc (Harry G. Hicks), $0.75
3016 Protactinium (H. S. Kirby), $1.00
3017 Iron (J. M. Nielsen), $0.50
3018 Manganese (G. W. Leddicotte), $0.50
3020 Rare Earths, Scandium, Yttrium, and Actinium (P. C. Stevenson and W. E. Nervik), $3.00
3021 Technetium (Edward Anders), $0.50
3022 Vanadium (J. L. Brownlee, Jr.), $0.75
3023 Tin (W. E. Nervik), $0.75
3024 Magnesium (A. W. Fairhall), $0.50
3025 Rare Gases (Floyd F. Momyer, Jr.), $0.75
3026 Mercury (J. Roesmer and P. Kruger), $0.50
3027 Copper (F. F. Dyer and G. W. Leddicotte), $0.75
3028 Rhenium (G. W. Leddicotte), $0.50
3029 Ruthenium (E. I. Wyatt and R. R. Rickard), $1.00
3030 Seenium (G. W. Leddicotte), $0.50
3031 Transcurium Elements (G. H. Higgins), $0.50

E. Roig, I. G. Rieckehoff, C. S. Russo, and **J. D. Curet**[1]
Puerto Rico Nuclear Center
University of Puerto Rico
Rio Piedras, P. R.

Radioisotope Demonstration of Common Ion Effect on Solubility

The commercial availability of many radioisotopes at microcurie levels which do not require that the purchaser possess an AEC license,[2] has placed new tools in the hands of chemistry teachers. Radioactive atoms behave chemically in essentially the same way as their stable isotopes, and their radiations are easily detectable; these facts make them excellent means for demonstrating chemical principles. Often a chemical analysis can be replaced by a simple radioactivity measurement with consequent saving of time and reagents. In other cases, it is possible to show better certain effects which are not so obvious when illustrated by conventional methods. The calculations necessary for the interpretation of results usually are very simple and straightforward. It is not necessary for the person who does the demonstration to be an expert in the field of radiochemistry. It is sufficient that he be acquainted with the basic techniques and precautions for handling radioisotopes.

This paper reports a direct demonstration of the effect of common ion concentration on the solubility of a uni-univalent salt, thallium(I) chloride. Thallium(I) chloride has been extensively used for solubility studies since the beginning of the century (*1*, *2*) and can be labeled either with chlorine-36 or with a thallium isotope. Thallium-204 was used here.

The Experiment

Thallium-204 can be obtained as thallium(I) nitrate in HNO_3 solution from Oak Ridge National Laboratory. The acidity of the solution is below 3*N* and the concentration of the activity not less than 1 mc/ml. Thallium-204 decays with a half life of 4.0 years by *beta* emission (maximum energy 0.765 Mev) and by electron capture (2%). Thallium(I) nitrate solution, 0.10*M*, is labeled by adding enough Tl-204 solution to 100 ml of 0.10*M* $TlNO_3$ so that the resulting solution has an activity from 1 to 5 microcuries per ml.

For the solubility study, the following solutions are convenient:

Solution 1, 0.60*M* KNO_3
Solution 2, 0.05*M* in $TlNO_3$ and 0.55*M* in KNO_3
Solution 3, 0.10*M* in $TlNO_3$ and 0.50*M* in KNO_3
Solution 4, 0.05*M* in KCl and 0.55*M* in KNO_3
Solution 5, 0.10*M* in KCl and 0.50*M* in KNO_3

The day before the demonstration is to be given, prepare the precipitate of thallium(I) chloride by placing in each of five conical 15-ml centrifuge tubes, 2 ml of 0.10*M* thallium(I) nitrate labeled with thallium-204 and 2 ml of 0.20*M* KCl solution. Let stand overnight.

On the following day, centrifuge the tubes, discard the supernatant, drain each tube well, and wash each precipitate with 1 ml of water. Centrifuge again, decant the supernatant, drain well. Add to first tube 1 ml of solution 1, to the second tube 1 ml of solution 2, to the third tube 1 ml of solution 3, to the fourth tube 1 ml of solution 4, and to the fifth tube 1 ml of solution 5. Shake each tube well after addition of the solutions and continue shaking the tubes in a regular pattern for at least 10 minutes. (It is better to use a shaking machine but it is not indispensable for semiquantitative results.) Centrifuge the tubes and measure an aliquot (50–200 λ) from each of the supernatants into polystyrene bases mounted on cardboard or aluminum. Dry under an infrared lamp, cover samples with cellophane, and count them in an end-window Geiger counter or a thin-window flow counter.

Precipitates are allowed to stand overnight in order to decrease the rate of isotopic exchange which is known to be lower for aged precipitates (*3*). The rate of isotopic exchange between the labeled solid thallium(I) chloride and thallium(I) ion in solution was found to be insignificant under the conditions of these experiments. Only 10 minutes are allowed for the precipitates to be in contact with the solutions with occasional stirring. These conditions were found to be satisfactory for saturation to be established yet to keep the time of the demonstration as short as possible.

It is evident however, that for more accurate results, not only a shaking apparatus but also a longer agitation period and a constant temperature bath are required. Also, solutions with common ion concentrations below 0.05*M* should be studied in order to include a larger number of points in the graphical treatment of the data.

The samples are dried before counting in order to minimize self-absorption effects. This takes from 5 to 10 minutes which might be used by the teacher to explain the operation of the counter and to obtain the background counting rate. The samples should contain enough activity so that counting for a short time (1 or 2 minutes) will give sufficient counts for good statistical significance.

After the samples are counted, the results can be tabulated on the blackboard and discussed. The explanations for the results obtained may be made as simple or rigorous as the level of student training permits.

A relatively high ionic strength, 0.6*M*, was chosen in order to neglect the contribution of the ions coming from the dissolution of the precipitate. Potassium nitrate was used as the inert salt because of its availability. However, since nitrate is known to associate somewhat with thallium(I) ion (*4*), perchlorate would be a better inert anion.

---

[1] Present address: Dean, Faculty of Natural Sciences, University of Puerto Rico.

[2] Nucleonic Corporation of America, 196 DeGraw St., Brooklyn 31, N. Y., supplies license-free amounts of several radioisotopes.

Some typical results obtained by the use of the method are presented in Table 1. In each case, aliquots of 0.10 ml were counted in a thin window flow proportional counter.

Table 1. Relative Solubilities of TlCl in the Presence of Cl^- Ion (Constant Ionic Strength = 0.60)

Solution	Number of samples	Arithmetic mean (cpm)	Per cent average deviation
0.60*M* KNO_3	4	13415	2
0.05*M* $TlNO_3$ + 0.55*M* KNO_3	6	6329	2
0.10*M* $TlNO_3$ + 0.50*M* KNO_3	5	4508	4
0.05*M* KCl + 0.55*M* KNO_3	6	6654	3
0.10*M* KCl + 0.50*M* KNO_3	6	4057	3

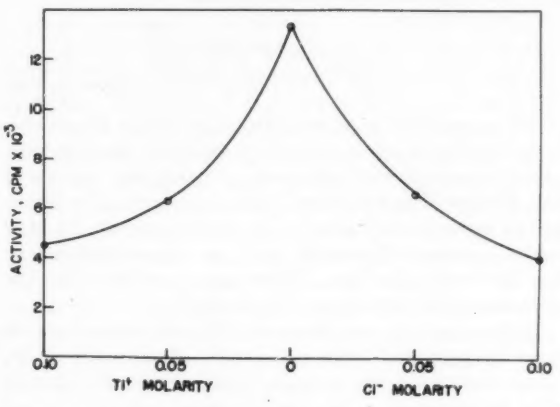


Figure 1. Relative solubilities of thallium(I) chloride in solutions of KCl and $TlNO_3$ with constant ionic strength.

Figure 1 shows the effect of increased common ion concentration on the solubility of TlCl. The similarity of the curves represented in Figure 1 is evidence that the common ion effect in depressing the solubility of uni-univalent salts is of the same order of magnitude for both the cation and anion, provided other equilibria are either absent or insignificant under the conditions considered.

The data can be interpreted quantitatively to show that it conforms to a simple equilibrium law and can be used to determine the value of Ksp. = (Tl^+) (Cl^-). Although it is known that additional equilibria such as $Tl^+ + Cl^- \rightleftharpoons TlCl$ solution and $TlCl + Cl^- \rightleftharpoons TlCl_2^-$ exist (*5*), they can be neglected under the conditions of the experiment. At ionic strength = 0.60, the equilibrium constant of the first has a value of approximately 1 and the second is still smaller. Therefore, at $(Cl^-) = 0.10M$ (the highest chloride concentration used in the experiment) only about 10% of the thallium in solution is present as undissociated TlCl.

Let A = measured activity of an aliquot of the supernatant (same volume aliquot in every case)

α = specific activity of solid in units such that A/α is the concentration of the Tl^+ which has appeared in the solution by dissolution of the solid

y = concentration of added Cl^-

z = concentration of added Tl^+

When Cl^- is the common ion, $K = (A/\alpha)(A/\alpha + y)$ or $A^2 = K\alpha^2 - \alpha Ay$.

When Tl^- is the common ion, assuming no exchange with the precipitate, $K = (A/\alpha + z)(A/\alpha)$ or $A^2 = K\alpha^2 - \alpha Az$.

In both cases, a plot of A^2 versus Ay or Az should be a straight line with intercept $K\alpha^2$ and slope $-\alpha$. Therefore, K can be calculated from this value, since K = intercept/slope^2. Figure 2 represents this treatment as applied to the experimental data. The chloride data falls excellently on a straight line and the thallium(I) data agrees with the same line as expected but shows more scatter. The line has an intercept of 1.80×10^8 and a slope of 4.1×10^5 giving a value of $1.07 \pm 0.2 \times 10^{-3}$ for K, the solubility product. The error assigned to K represents the extremes of the thallium(I) data. From this value, the solubility of TlCl at room temperature (approximately 28°C) is found to be 0.033 moles per liter. No data is available for the solubility of TlCl under the conditions used in this experiment. By making certain rough interpolations using data from Seidell (*6*) the solubility of TlCl under these conditions was estimated as 0.030 mole per liter. This value shows a good agreement with the experimental value considering the nonrigorous control of conditions in a demonstration experiment.

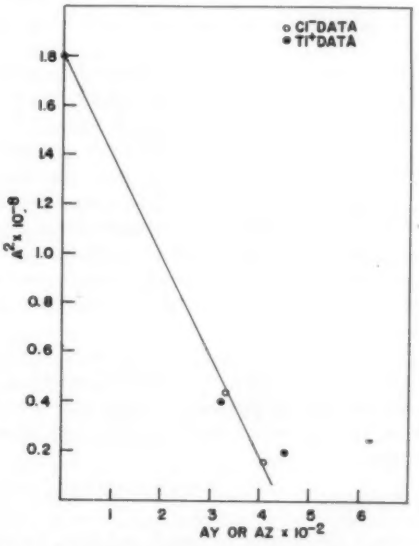


Figure 2. Graphical determination of solubility product.

We are indebted to Prof. R. W. Dodson, Chairman of the Chemistry Department of Brookhaven National Laboratory, for his suggestions concerning the presentation and the interpretation of the data.

Literature Cited

(1) Bray, William C., and Winninghoff, W. J., *J. Am. Chem. Soc.*, **33**, 1663 (1911).
(2) Bray, William C., *J. Am. Chem. Soc.*, **33**, 1673 (1911).
(3) Kolthoff, I. M., and Rosenblum, Charles, *J. Am. Chem. Soc.*, **56**, 1658 (1934).
(4) Nair, V. S., and Nancollas, G. H., *J. Chem. Soc.*, **1957**, 318.
(5) Hu, K. H., and Scott, A. B., *J. Am. Chem. Soc.*, **77**, 1380 (1955).
(6) Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed., D. van Nostrand Co., Inc., New York, 1940, Vol. 1, p. 1547.

D. J. Carswell
Department of Nuclear and
Radiation Chemistry
University of New South Wales
Kensington, Sydney, Australia

Convenient Radioactivity Sources

In an earlier paper,[1] methods for the preparation of α-sources were reviewed and a new method for α-source preparation was described. It is the purpose of this paper to describe a method which has been devised for the preparation of mechanically robust and chemically inert β- and γ-sources for teaching purposes. The method is cheap, simple, and readily applicable to large-scale production. The sources are also suitable as reference sources for checking monitoring equipment.

The process consists of incorporating a suitable radioactive isotope of an element, or a compound of the element, as the filler in an epoxy resin/hardener mixture which is then cast into molds and allowed to set. Resins which have been found suitable for this process are Shell Chemical Co. resin type 828 and Ciba Araldite type D.

In order to obtain best results it was found desirable to mix the radioactive compound slowly into the resin before adding the hardener. Rapid mixing, which is necessitated by adding the radioactive material after the hardener, results in aeration and less attractive sources. Warming the resin reduces its viscosity and permits easier mixing but high temperatures should be avoided. The resin/filler/hardener mixture can be conveniently measured and dispensed into conventional aluminum source planchets with a dropping pipet and allowed to set.

If it is desired, alternative molds may be employed to provide special shapes for specific needs, e.g., the inverse square law experiment which for best results requires a symmetrical source in the end of an aluminum peg.

Source Materials

β-sources. The material which has been found most satisfactory for the preparation of β-sources is yellow uranium trioxide obtained by thermal decomposition of uranyl nitrate at 350°C. Uranium-238 is itself an α-emitter which rapidly establishes equilibrium with its first two daughters, both β-emitters:

$$U^{238} \xrightarrow[4.5 \times 10^9 \text{ yrs}]{\alpha} Th^{234} \xrightarrow[24.1 \text{ d}]{\beta(0.19 \text{ Mev})}$$

$$Pa^{234} \xrightarrow[1.18 \text{ m}]{\beta(2.3 \text{ Mev})} U^{234} \xrightarrow[2.5 \times 10^5 \text{ yrs}]{\alpha}$$

All α particles as well as the low energy β-particles from the Th^{234} are absorbed by the resin mixture thus providing a source of high energy β-particles. By use of the Bleuler-Zünti method,[2] the experimentally determined energy was found to be approximately 2.3 Mev which compares favorably with the theoretical energy for Pa^{234} of 2.31 Mev. There is no evidence of the presence of the low energy β from the Th^{234}.

Approximately one thousand 0.01 microcurie sources may be prepared from one ounce of uranium oxide, thus illustrating the economy with which the sources may be prepared.

Other β-emitting isotopes may of course be used, but for our purpose uranium oxide has been found most convenient.

γ-sources. The most satisfactory material for the preparation of γ-sources is undoubtedly cobalt-60 in the form of low specific activity oxide. Cobalt-60 decays by β-emission (0.31 Mev) to Nickel-60 with the emission of two γ-rays (1.33 Mev and 1.17 Mev). The β-particles are of such low energy that they are readily absorbed by the resin mixture and thus produce what is virtually a pure γ-source suitable for all introductory experiments (range, penetration studies, detector characteristics, etc.) and also for some of the more advanced experiments such as γ spectrometry.

[1] Carswell, D. J., and Milsted, J., *J. Nuclear Energy*, **4**, 51 (1957).

[2] Segrè, E., "Experimental Nuclear Physics," John Wiley and Sons, Inc., N. Y., Chapman and Hall Ltd., London, **1953**, Vol. 1, p. 298.

Who Am I?

I have no Gly and I have no Glu,
My amino-terminal group is Leu.
On hydrolysis I give two other acids:
One, with hydroxyl, is aliphatic;
The other, *sans*-hydroxyl, is very aromatic.
The group at the carboxy end of the chain
Rhymes with a syllable in my real name.

Found on a Harvard Chem 20 exam.

(*See page 362*)

The Basis for a New Conception of an Electrode Potential

Escaping tendency of electrons in the electrode of electrode systems at equilibrium

J. B. Ramsey
University of California
Los Angeles

The definition of an electrode potential given in this paper is essentially different in meaning from that of either of the two definitions in current usage.[1] A large number of chemists, including European chemists in general, all electrochemists, and many American biological and analytical chemists, have adopted the unequivocal definition of an electrode potential in which the term "potential" is used in its electrostatic sense. On the other hand most American physical chemists have apparently concurred in the treatment of electrode potentials first proposed by G. N. Lewis (*1*) and now presented in substantially all American-authored textbooks in chemistry (first year chemistry, quantitative analysis, physical chemistry, and chemical thermodynamics). In this treatment the term potential is not used in its generally accepted sense; nor is it applied directly to an electrode. These peculiarities in the Lewis treatment have been confusing to many chemists. Private communications from a considerable number of reputable physical chemists in this country and in Europe fully substantiate this opinion.

It may be well to state beforehand that in the definition of the potential of an electrode to be given, the term potential is used in its thermodynamic sense, and is directly applicable to an electrode. Also, from electrode potentials, so defined, the thermodynamic origin of the voltage of a voltaic cell is directly and intuitively recognized.

The derivation of such a definition has been presented previously (*2*) for the consideration of a rather limited group of specialists. This paper has been written with the intention of presenting the development of this new conception in such a way that it might prove to be of interest and value to a wider group of chemists, in particular to those whose principal concern is with the presentation of this subject to students.

Voltaic Cells and Electrode Systems

A voltaic cell, as ideally conceived, consists of two electrode systems, each at equilibrium within itself and both at the same temperature. The term "electrode system" applies to any heterogeneous chemical system in which the electron is one of the chemical substances involved.[2] As a consequence such a system must consist of a substance, or set of substances, which exists in what is commonly referred to as the "reduced" state along with a conjugate set of substances referred to as the "oxidized" state.

Expressions for the Equilibria Existing in Electrode Systems

An electrode system at equilibrium is to be treated in the same way as any system at equilibrium at a certain temperature and pressure. The significant chemical equilibrium existing in each of three well-defined (and somewhat typical) electrode systems is considered. Incidentally it is known that equilibrium is attained in each of these systems in a conveniently short time after the system is prepared.

(1) The zinc-zinc ion (Zn, Zn^{++}) electrode system consists of a piece of zinc dipping into (in contact with) a certain aqueous solution of a zinc salt at 25°C and one atmosphere. In this system metallic zinc is the only substance in the "reduced state." The conjugate set of substances in the "oxidized state" is the Zn^{++}, primarily in the zinc salt solution, plus the electron, primarily in the zinc electrode.[3]

The expression for the significant chemical equilibrium existing in this system is

$$\text{Zn (solid)} \rightleftharpoons \text{Zn}^{++}\text{ (in the solution)} + 2e^{-}\text{ (in the Zn electrode)}$$

(2) The iron(II)-iron(III) (Fe^{+2}, Fe^{+3}) electrode system consists of a piece of platinum (or other suitable noble metal) in contact with an aqueous solution containing an iron(II) and an iron(III) salt, each at a definite concentration. Iron(II) ion in the solution constitutes the "reduced state" and the iron(III) ion in the solution plus the electron in the

[1] In this paper the meaning of the term "potential" in the designation "electrode potential" is not restricted to its electrical (or electrostatic) meaning. It is realized that this lack of restriction on the meaning of potential in this designation is not in accordance with the recommendations of the Commission on Physico-Chemical Symbols and Terminology and of the Commission on Electrochemistry of the I.U.P.A.C. at its meeting in Stockholm in 1953. For the most recent publication of the recommendations of these Commissions see the *J. Am. Chem. Soc.*, **82**, 5517 (1960).

[2] For a discussion of the appropriateness of the treatment of the electron in these systems in the same way as that of an ordinary chemical substance, see EASTMAN, E. D., AND ROLLEFSON, G. A., "Physical Chemistry," McGraw-Hill Book Co., Inc., New York, **1947**, pp. 438–440.

[3] The use of the adverb "primarily" is theoretically (if not practically) necessary since an infinitesimal fraction of the total zinc ion in this system is considered to exist in the Zn electrode, and a quite undetectable fraction of the mobile electrons in this system is properly conceived as existing in the aqueous phase. It may be noted that the mobile electrons in any electrode system exist primarily in the metallic phase, the electrode of that system, at least if water is the solvent medium.

electrode, the "oxidized state." The significant chemical equilibrium in this system is

$$Fe^{+2}\text{ (in the solution)} \rightleftharpoons Fe^{+3}\text{ (in the solution)} + e^{-}\text{ (in the electrode)}$$

(3) The electrode system consisting of silver and silver chloride in contact with a certain aqueous solution of a soluble chloride (referred to as the Ag, Cl^-, AgCl system) contains solid silver plus Cl^- (in the solution) in the "reduced state" and solid AgCl plus electrons (in the Ag electrode) in the "oxidized state." The expression for the equilibrium existing therein is

$$Ag(s) + Cl^{-}\text{ (in the solution)} \rightleftharpoons AgCl(s) + e^{-}\text{ (in the Ag electrode)}$$ [4]

Relations Between the Escaping Tendencies of the Constituents of an Electrode System at Equilibrium

The conception of escaping tendency was introduced in chemical thermodynamics by G. N. Lewis (*3*). The most fundamental thermodynamic measure of this property of a substance at a certain temperature and pressure is its free energy per mole, which is designated its partial molar free energy, $\bar{F}$, if present in a solution, and its molar free energy, $\tilde{F}$, when existing in the pure state.

According to the basic criterion for the existence of equilibrium in a system kept at constant temperature and pressure, the system will undergo no change in free energy during any imaginable infinitesimal displacement (or reaction) in the system (or finite reaction in an infinite copy of the system). Consequently the relations between the escaping tendencies of the substances involved in each of the three electrode systems (listed above) are respectively:

(*a*) $\tilde{F}_{Zn} = (\bar{F}_{Zn^{++}})_{\text{in the solution}} + (\bar{F}_{e^-})_{\text{in the Zn electrode}}$

(*b*) $(\bar{F}_{Fe^{+2}})_{\text{in the solution}} = (\bar{F}_{Fe^{+2}})_{\text{in the solution}} + (\bar{F}_{e^-})_{\text{in the Pt electrode}}$

(*c*) $\tilde{F}_{Ag} + (\bar{F}_{Cl^-})_{\text{in the solution}} = \tilde{F}_{AgCl} + (\bar{F}_{e^-})_{\text{in the Ag electrode}}$

It is seen that in each of these electrode systems (at equilibrium at a certain temperature and pressure) the escaping tendency of the electron (as measured by $\bar{F}_{e^-}$) in the electrode is determined solely by the composition of the solution in that system.[5] In general the partial molar free energy of an ionic species increases with increase in its concentration over a rather wide range of concentration (not linearly except at very low concentrations).

Thermodynamic Origin of the Voltage of a Voltaic Cell

The existence of the voltage of any voltaic cell is thermodynamically attributable to the fact that the escaping tendency of the electron in one of the electrodes (at equilibrium in its electrode system) is greater than in the other electrode (at equilibrium in its electrode system). When, therefore, a path is provided whereby the electron may pass from one electrode to the other it will do so spontaneously from that electrode in which the electron has the higher escaping tendency (the greater value of $\bar{F}_{e^-}$) to the one with the lower escaping tendency. Such a path is provided when the two electrodes are connected by a metallic conductor.

It follows that the voltage of a cell should be expressible directly in terms of the escaping tendencies of the electron in its two electrode systems. The particular voltaic cell consisting of the two electrode systems, Fe^{+2}, Fe^{+3} and Ag, Cl^-, AgCl, will be used for the purpose of illustrating the reasoning involved in obtaining the expression for this relation. This cell may be formulated,

$$[Pt,\ Fe^{+2}\text{ (at } m_{Fe^{+2}}),\ Fe^{+3}\text{ (at } m_{Fe^{+3}})],\ [Cl^-\text{ (at } m_{Cl^-}),\ AgCl,\ Ag] \quad (A)$$

where m_i represents the actual molality of the ith ion in the electrode system (at equilibrium) in which it exists.

Consider the chemical change occurring in each of the electrode systems *per faraday* of electrons passed *reversibly* through the outer metallic circuit (such as copper) from the Pt electrode to the Ag electrode (at constant T and p). (This may or may not be the direction in which the passage of the electrons will occur spontaneously.) This reversible transfer of electrons will be accompanied by the oxidation of one mole of Fe^{+2} (at $m_{Fe^{+2}}$) to Fe^{+3} (at $m_{Fe^{+3}}$) in the Fe^{+2}, Fe^{+3} electrode system at equilibrium, and by the transformation (a reduction) of one gram formula weight of AgCl into Ag and Cl^- (at m_{Cl^-}) in the Ag, Cl^-, AgCl system at equilibrium.

The over-all isothermal change in state in this idealized cell, per faraday of electrons so passed, is the resultant of the following simultaneous changes in state:

(*a*) $Fe^{+2}\text{ (at } m_{Fe^{+2}}) \rightarrow Fe^{+3}\text{ (at } m_{Fe^{+3}}) + e^-\text{ (in Pt electrode)}$. Since this change in state occurs in the Fe^{+2}, Fe^{+3} electrode system *at equilibrium* the value of the change in free energy, ΔF_a, which accompanies it is zero.

(*b*) $e^-\text{ (in Pt electrode)} \rightarrow e^-\text{ (in Ag electrode)}$

$$\Delta F_b = (\bar{F}_{e^-})_{\text{in Ag electrode}} - (\bar{F}_{e^-})_{\text{in Pt electrode}}$$

(*c*) $e^-\text{ (in Ag electrode)} + AgCl \rightarrow Ag + Cl^-\text{ (at } m_{Cl^-})$

$\Delta F_c = 0$ for same reason that $\Delta F_a = 0$.

The change in state resulting from these three simultaneous changes is seen to be:

$$Fe^{+2}\text{ (at } m_{Fe^{+2}}) + AgCl \rightarrow Fe^{+3}\text{ (at } m_{Fe^{+3}}) + Ag + Cl^-\text{ (at } m_{Cl^-}) \quad (I)$$

The electron is not involved in this over-all change since there is no *resultant* change in the electron content of either electrode (the Pt or the Ag). Since the summation of the ΔF's accompanying the three component changes gives the value of the resultant change in free energy, ΔF_I, it follows that:

$$\Delta F_I = \Delta F_a + \Delta F_b + \Delta F_c = \Delta F_b = (\bar{F}_{e^-})_{\text{in Ag electrode}} - (\bar{F}_{e^-})_{\text{in Pt electrode}} \quad (1)$$

The magnitude of the value of ΔF_I is seen to be determined by the magnitude of the difference between the escaping tendencies of the electron in the two electrodes.

It may be recalled that the change in free energy accompanying an isothermal change in state which can occur reversibly in a voltaic cell is equal in magnitude and opposite in sign to that of the maximum

---

[4] In order to avoid any possible misinterpretation of these three equilibrium expressions it may be well to note that each of them may be written with equal correctness and significance in the reverse order, i.e., with the substances in the "oxidized state" on the left of the equilibrium sign, and those in the "reduced state" on the right.

[5] Had not the electrodes in systems (1) and (3) been restricted to the pure metals, Zn and Ag respectively, the composition of the electrode would have been an additional factor determining the value of $\bar{F}_{e^-}$ in each of these electrode systems.

(reversible isothermal) electrical work, $W_{rev.\ el.}$, that can be *done on* the surroundings (of the cell) during the specified change in state,[6] i.e., $\Delta F = -W_{rev.\ el.}$ The numerical value (magnitude) of $W_{rev.\ el.}$ is given by that of the product $n\mathfrak{F}E$ where E is the cell voltage, n the number of faradays involved (required by the isothermal change in state considered), and $\mathfrak{F}$ the faraday in coulombs. It is seen that the sign to be given to $W_{rev.\ el.}$, that is to $n\mathfrak{F}E$, is determined *solely* by the sign of ΔF accompanying the isothermal change in state which is being considered. It follows that the sign of the value of $n\mathfrak{F}E$ is entirely independent of the arbitrary way in which the cell may be formulated on a plane surface (horizontally, perpendicularly, or otherwise). The adoption of a sign convention for expressing the value of the voltage, E, of a cell, which is determined by the way the cell may be formulated horizontally on a plane surface,[7] has in the opinion of the author beclouded the essential characteristics of the thermodynamics involved in the consideration of voltaic cells. This confusion is obviated by recognizing the value of the voltage, E, of any cell to be a property of the cell having *magnitude without sign* (entirely independent of the arbitrary way in which the cell may be formulated).[8] An attempt has been made elsewhere (*4*) to give more ample justification for this conclusion, namely that the adoption of a sign convention for expressing the value of the voltage of a cell, dependent on its formulation, is confusing and misleading and should, therefore, be discontinued. Such a sign convention is not involved in the development to follow.

For the change in state to be considered [relation (I) above] we have

$$W_{rev.\ el.} = n\mathfrak{F}E = -\Delta F_I \qquad (2$$

in which the magnitude of $n = 1$, and its sign is determined by the sign of ΔF_I (a negative sign if $\Delta F_I > 0$, and a positive sign if $\Delta F_I < 0$).

From equations (1) and (2) it is seen that

$$\Delta F_I = -(n\mathfrak{F}E_A) = (\bar{F}e^-)_{\text{in Ag electrode}} - (\bar{F}e^-)_{\text{in Pt electrode}} \qquad (3)$$

where E_A is the voltage of Cell A formulated above. It is known that at any ordinary temperature (such as 25°C) silver will react *quite completely* with iron(III) ion and chloride ion (in a solution containing each of these ions at any ordinary molalities) to form silver chloride and iron(II) ion. Work must therefore be done on Cell A during the change in state considered [formulated by (I) above]; whence it follows that n will be equal to -1. Since the voltage of any cell, as we conceive it, is a property of a cell which has a positive value only, it follows from Equation (3) that

$$\overset{E}{\text{Cell A}} = \left| \frac{(\bar{F}e^-)_{\text{in Pt electrode}}}{\mathfrak{F}} - \frac{(\bar{F}e^-)_{\text{in Ag electrode}}}{\mathfrak{F}} \right| \qquad (4)$$

where the perpendicular lines indicate the numerical (not algebraic) value of the right hand member of this equation. The general conclusion warranted by this equation is that the magnitude of the voltage of any cell is determined by the magnitude of the difference between the escaping tendencies of the electron in its two electrodes (each in their respective electrode systems at equilibrium).

The Thermodynamic Potential of an Electrode; Its Magnitude and Sign

The general form of Equation (4), which is applicable to any cell consisting of any two electrode systems, j and k, is

$$E = \left| \frac{(\bar{F}e^-)_j}{\mathfrak{F}} - \frac{(\bar{F}e^-)_k}{\mathfrak{F}} \right| \qquad (5)$$

It is apparent that the quantity $(\bar{F}e^-)/\mathfrak{F}$ represents for each electrode an intensive thermodynamic property of that electrode. This thermodynamic property is a potential in volts. A distinguishing name and symbol for this potential of an electrode is needed if confusion is to be avoided. The symbol chosen for $(\bar{F}e^-)_i/\mathfrak{F}$ is $\mathcal{E}_i$ and the name is "electron chemical potential."[9]

---

[6] This relation between ΔF and $W_{rev.\ el.}$ is in accordance with the sign convention presently adopted for expressing the value of W by most American and some European physical chemists, namely, that the value of W be given a positive sign if work is done on the surroundings during a specified process for bringing about the change in state considered and a negative sign if done on the system.

[7] Such a sign convention for expressing the value of E, first proposed by G. N. Lewis (*1*), has been recommended by the International Commissions of I.U.P.A.C., referred to in footnote 1. This sign convention is and has been quite widely used. It may be briefly stated in the following way: The voltage, E, of a cell, as formulated horizontally on a plane surface, shall be given a positive sign if electrons will flow spontaneously from the left hand electrode to the right hand electrode through the outer metallic circuit when these electrodes are connected by a metal; or a negative sign if the spontaneous flow of electrons is in the opposite direction. It should be noted that this sign convention is not applicable to an actual voltaic cell (such as a lead storage battery or a dry cell); *only* to a horizontal formulation of the cell on a plane surface.

[8] The confusion, referred to, arises when it is made to seem (as so often happens) that the sign of $n\mathfrak{F}E$ is in some way dependent on the relative positions arbitrarily assigned to the two electrode systems in the horizontal formulation of the cell involved. Such dependence does not exist; nor should it be inferred that it does. If the voltage, E, of every cell is to be given a positive value *only* the following question may arise: "How then can the useful information about a cell as formulated (which is given by the sign convention widely used in expressing the value of E) be provided without recourse to a sign convention for E?" This information can be readily provided without confusing the thermodynamic treatment of voltaic cells by merely drawing an arrow parallel to the formulation of the cell (however it may be formulated, horizontally, perpendicularly or otherwise) which shows the direction of spontaneous flow of electrons through the outer circuit.

The following illustration may help to clarify this unorthodox point of view. Consider an idealized voltaic cell consisting of the two electrode systems, Zn, Zn^{++}, and Cu, Cu^{++}, in which the Zn^{++} and the Cu^{++} are each in their hypothetical standard states, that is, at an effective molality equal to one. On the basis of well-known facts about these two electrode systems it is concluded that the voltage of this idealized cell is equal to 1.100 volts (positive sign understood) regardless of the way in which it may be formulated. Either of the two following horizontal formulations of this cell will give adequate and non-misleading information about this cell:

$$\overrightarrow{[Zn,\ Zn^{++}(ss)],\ [Cu,\ Cu^{++}(ss)]} \qquad (a)$$

or

$$\overleftarrow{[Cu,\ Cu^{++}(ss)],\ [Zn,\ Zn^{++}(ss)]} \qquad (b)$$

where *ss* symbolizes the standard state. The arrows show the direction in which electrons will flow spontaneously through the outer metallic circuit. As stated above, $E_a = E_b = 1.100$ volts.

[9] This name seems meaningful and unambiguous since the designation "chemical potential" is and has been used by many physical chemists for that intensive thermodynamic property which we have called "partial molar free energy," following G. N. Lewis.

To be able to assign a unique numerical value to the electron chemical potential, $\mathcal{E}$, of any electrode (in its electrode system at equilibrium) *it is necessary* to adopt arbitrarily a certain numerical value for the $\mathcal{E}$ of some well-defined electrode system. This is a consequence of the fact that only differences between potentials of any kind are definable in terms of physical realities (cell voltages in the case of $\mathcal{E}$-values). In accordance with the universal practice followed in the treatment of electrode potentials (regardless of their definition) the so-called standard hydrogen electrode system *at equilibrium* (an hypothetical H_2, H^+ electrode system) is chosen as the reference electrode system[10] and *the value arbitrarily adopted* for the chemical potential (partial molar free energy) of the electron in the electrode of this system is *zero*.

Thus to obtain the magnitude (*not the sign*) to be given to the $\mathcal{E}$-value of any electrode system, i, it is necessary to determine the voltage, E, of the voltaic cell which consists of the two electrode systems, viz., the standard hydrogen electrode system (the $\mathcal{E}$-value of which to be symbolized $\mathcal{E}_{H_2}°$) *and* the ith electrode system since for this cell Equation (5) becomes

$$E = |\mathcal{E}_i - \mathcal{E}_{H_2}°| = |\mathcal{E}_i| \qquad (6)$$

The sign to be given to $\mathcal{E}_i$ depends on the direction in which electrons would flow spontaneously between the electrodes of these two electrode systems, that is, by the relative magnitude of the escaping tendency of the electron in the ith electrode to its escaping tendency in the electrode of the standard hydrogen electrode system (each of these systems being at equilibrium).[11] It is seen that if $\mathcal{E}_i$ is numerically greater than $\mathcal{E}_{H_2}°$, the sign to be given $\mathcal{E}_i$ is positive; if numerically less than $\mathcal{E}_{H_2}°$, its sign will be negative. It may be recalled that

$$\mathcal{E}_i \; [\equiv (\bar{F}_{e^-})_i/\mathfrak{F}]$$

is an intensive thermodynamic property of the ith electrode system at equilibrium. It is seen that its sign and magnitude are determined *solely* by the nature and state of the ith electrode system; entirely independent of the nature of the other electrode system with which it may be associated in a voltaic cell or the way that cell may be formulated.[12]

The electron chemical potential of any electrode system in which all the substances involved in that system, except the electron, exist in their standard states is known as its standard electron chemical potential, symbolized by $\mathcal{E}_i°$. The $\mathcal{E}$-value of any non-standard electrode system, $\mathcal{E}_i$, can be readily shown to be related to its standard value, $\mathcal{E}_i°$, by the equation

$$\mathcal{E}_i = \mathcal{E}_i° - (RT/n\mathfrak{F}) \ln (\text{Ox})/(\text{Red})$$

where n is the number of faradays involved (for example n equals two for the Zn, Zn^{++} system, one for the Fe^{+2}, Fe^{+3} system, etc.); (Red) represents the product of the mass action effects of the substances in the "reduced state," each raised to its appropriate power, and (Ox) that of the substances, other than the electron, in the "oxidized state."

It may be noted that the value of $\mathcal{E}_i$ of any electrode system *et equilibrium* is determined by the tendency of the substances constituting the "reduced states" to change to the substances (other than the electron) constituting the "oxidized state," *and* to electrons in the state in which they exist in the electrode of the standard hydrogen electrode system at equilibrium. The greater this tendency the greater will be the algebraic value of $\mathcal{E}_i$.

In their comprehensive article on electrode potentials, Licht and de Béthune (*5*) have given a thorough discussion of the two meanings of electrode potentials now being used (referred to in the first paragraph in this paper) along with a comparison of those definitions with that of the electron chemical potential, $\mathcal{E}$, of an electrode as defined herein. An analysis of the Lewis treatment of electrode potential has also been given by the author (*4*).

Literature Cited

(1) Lewis, G. N., and Randall, M., "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, **1923**, pp. 402–404.
(2) Ramsey, J. B., *J. Electrochem. Soc.*, **104**, 255 (1957).
(3) For a clarifying discussion of the meaning and evaluation of the escaping tendency of a substance see Reference (1), Chap. 27.
(4) Ramsey, J. B., *J. Electrochem. Soc.*, **104**, 691 (1957).
(5) Licht, T. S., and de Béthune, A. J., J. Chem. Educ., **34**, 433 (1957).

[10] It may be noted that this reference electrode system is a very well defined system which is hypothetical in that the standard states of H_2 and of H^+ are defined states which cannot be actually produced. Nevertheless, this system can be used unequivocally in deriving $\mathcal{E}$-values of other electrode systems.

[11] If the direction of spontaneous electron flow is not apparent from previous knowledge of the direction in which the resultant chemical change involved in the cell tends to occur (takes place with a decrease in free energy) it may be determined directly by use of a voltmeter. This direction will, of course, be shown by the electrical circuit required in the potentiometric measurements of the voltages of cells which is used in obtaining the voltage of any idealized cell.

[12] A large number of chemists (referred to in the first paragraph of this article) have adopted the definition of an electrode potential in which the term potential is used in its electrostatic sense (commonly designated by V). It is a necessary consequence of this definition that the $\mathcal{E}$-value of any electrode system shall be equal in magnitude and opposite in sign to its V-value, i.e., $\mathcal{E}_i = -V_i$. For example:

$$\mathcal{E}°_{Zn,\ Zn^{++}} = +0.763 \text{ volt}; \quad V°_{Zn,\ Zn^{++}} = -0.763 \text{ volt}$$

Reservations for Copies of New CHEM Study Texts

To reserve examination copies of the revised CHEM Study text and lab manual at net cost (estimated at $5.00), mail name and address to CHEM Study, Harvey Mudd College, Claremont, California, before August 1. Books will be mailed when all volumes are completed about February 1, 1962. (Books will not be available for trial in schools other than those selected by CHEM Study to participate in its 1961 summer institutes.)

Boleslaw Ludwik Dunicz[1]
The Kosciuszko Foundation
New York City

Surface Area of Activated Charcoal by Langmuir Adsorption Isotherm

The study of the Langmuir adsorption isotherm of acetic acid by activated charcoal, offered in a basic physical chemistry course, involves plotting the relevant data and finding the corresponding constants. The purpose of this paper is to suggest an interpretation of the experimental data to make the exercise more meaningful for the student. This is the estimation of the specific adsorption area of charcoal.

For the adsorption of acid from its aqueous solution, the Langmuir isotherm can be expressed as:

$$C/X = a + bC \qquad (1)$$

where

- C = concentration of acetic acid solution, in moles/liter, which is in dynamic equilibrium with acetic acid adsorbed on the charcoal,
- X = number of moles of acetic acid adsorbed by one gram of charcoal, when the solution in contact with it has the equilibrium concentration C; the units of X are moles/g, where g = gram of dry charcoal,
- a = constant; its units are the same as those of C/X,
- b = constant; its units are g/mole.

Figure 1 shows a plot of X with respect to C, for room temperature, with "Norit A" charcoal used as an adsorbent. The experimental techniques were similar to those outlined in various physical chemistry laboratory manuals (*1*).

Figure 2 shows a plot of C/X values with respect to C. The straight line, drawn according to the linear regression method, fits the data. Hence it can be inferred that the acetic acid molecules, within the indicated concentration range, form a monomolecular layer on the surface of charcoal.

The constants a and b of the Langmuir isotherm represent the intercept and the slope respectively, of the line drawn in Figure 2.

The isotherm implies that as the values of C become larger, the contribution of the constant a to the value of C/X becomes negligibly small. Thus:

$$\lim C/X = bC \qquad (2)$$

Cancellation of C terms, and taking the recriprocal of equation (2), gives

$$\lim X = X_{max} = 1/b \qquad (3)$$

The X_{max} denotes the maximum capacity, in moles of acetic acid, which can be held by one gram of charcoal as a monomolecular layer.

According to Hansen and Craig (*2*), the adsorption by nonporous carbons of various aliphatic normal monocarboxylic acids from their aqueous solutions, up to an activity of 0.1, is independent of molecular weight but related to the absolute activity. Hence it may be assumed that molecules of such acids, on the charcoal surface, would be oriented vertically in closely packed

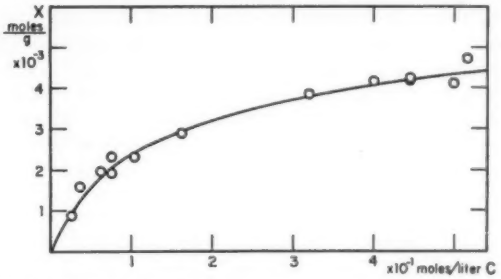


Figure 1. Number of moles of acetic acid adsorbed by one gram of "Norit A" activated charcoal with respect to the equilibrium concentration of aqueous acetic acid solution, at room temperature.

monomolecular layers. The cross-section of the acids is known to be 21 Å² (*3*). The foregoing information, and the experimentally determined constant b of the Langmuir isotherm, permits then an estimation of the specific area, S:

$$S = (1/b) \times N \times 21 \times 10^{-20}\ (\text{meters})^2 \qquad (4)$$

where N stands for the Avogadro number.

Example:

The reciprocal of the slope of the plot in Figure 2 is

$$1/b = \Delta C/\Delta(C/X) = 5.33 \times 10^{-3}\ \text{mole/g}$$

Hence:

$$S = 5.33 \times 10^{-3}\ (\text{moles/g}) \times 6.023 \times 10^{23}\ (\text{molecules/mole}) \times 21 \times 10^{-20}\ (\text{m}^2/\text{molecule})$$
$$= 6.74 \times 10^{2}\ \text{m}^2/\text{g}$$

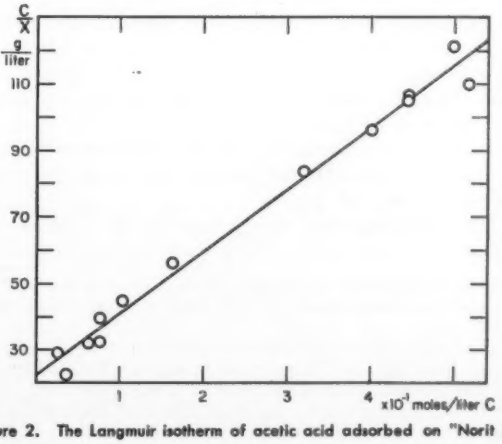


Figure 2. The Langmuir isotherm of acetic acid adsorbed on "Norit A."

[1] Present address, U. S. Naval Radiological Defense Laboratory, San Francisco 24, California.

The above result is in close agreement with the mean surface area of 708 m^2/g of the activated charcoal distributed by the Fisher Scientific Company. Brunauer, Emmett, and Teller (*4*) derived this number from adsorption studies with nitrogen and other gases, using the molecular cross-sectional areas calculated from the solid state. The value checks also very well with the figures of the American Norit Company, Inc., which reports that the total internal surface of Norti A (according to B.E.T. method, calculated from the benzene adsorption isotherm at 20°C) usually runs between 600–700 m^2/g dry carbon.

In addition, the information contained in the work of Hansen and Craig (*2*) discloses that measurement of the charcoal surface area might offer a potential approach to estimate certain dimensions of different substances, providing certain limitations to the activity are observed. Thus the purpose of the experiment might be extended to measure the dimensions of various water-soluble substances, such as oxalic, boric, arsenic, picric, or salicylic acid, to mention but a few. Acetic acid could then be used as a convenient reference material, since it is readily available and easily handled, and its molecular cross-section is known. If the Langmuir isotherm holds, the equation for finding the dimension, D, of another substance, using acetic acid as reference, is:

$$D = b_D/b_A \times 21 \text{ Å}^2 \qquad (5)$$

where b_A and b_D are the relevant constants (in g/mole) of the Langmuir isotherm, determined under identical experimental conditions, for the acetic acid and another substance, respectively.

Literature Cited

(1) Livingston, Robert, "Physico Chemical Experiments," 3rd ed., The Macmillan Co., New York, **1957,** pp. 257–9; Daniels, Farrington, et al., "Experimental Physical Chemistry," 5th ed., McGraw-Hill Book Co., New York, **1956,** pp. 226–7; and Steinbach, Otto F., and King, Cecil V., "Experiments in Physical Chemistry," American Book Co., New York, **1950,** p. 214.

(2) Hansen, Robert S., and Craig, Roy P., *J. Phys. Chem.*, **58,** 211 (1954).

(3) Rutgers, A. G., "Physical Chemistry," Interscience Publishers, Inc., New York, **1954,** p. 27; Moore, Walter J., "Physical Chemistry," 2nd ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., **1955,** p. 510; and Glasstone, Samuel, "The Elements of Physical Chemistry," D. Van Nostrand Co., Inc., New York, **1946,** p. 556.

(4) Brunauer, S., et al., *J. Am. Chem. Soc.*, **60,** 309 (1938).

Gerald Perkins, Jr., J. W. Wimberley, J. F. Lamb, and **L. E. Maurer**
North Texas State College
Denton

The Turbidimetric Determination of Lead

An inspection of current textbooks of instrumental analysis indicates that the turbidimetric method is still of sufficient importance to be included in the usual college course. Not only do these books give a theoretical discussion of this method of analysis but they also include one or more laboratory experiments designed to acquaint the student with both the application of the method and the adaptation of a variety of optical instruments for use with the technique. Unfortunately, most turbidimetric analyses require some extreme precautions to insure proper reproducibility of results.

The turbidimetric determination of sulfate ion, an experiment found in most current textbooks of instrumental analysis, is a case in point. For this determination the reagent must be sifted and used in the solid form. Additives must be introduced to maintain a proper suspension. Mixing the various ingredients calls for elaborate procedures involving either a constant rate of shaking or precise intervals of agitation. Time is an important factor throughout and time intervals between manipulations must be reproduced almost exactly.

This emphasis upon exact reproduction of conditions from experiment to experiment undoubtedly acquaints the student thoroughly with the need for extreme care and attention to detail which characterizes many turbidimetric analyses. On the other hand, the student is very often even more thoroughly impressed and discouraged by the relatively poor results obtained in this first encounter, poor results which come after what seems a disproportionate amount of tedious work. The very quantity of necessary direction and precaution usually overwhelms even the best student, so that

Presented before the 1st Annual Student Meeting-in-Miniature, Dallas-Fort Worth Section of the ACS, Denton, Texas, May, 1960.

The authors wish to express their gratitude to the Faculty Research Fund of North Texas State College for financial support granted the undergraduate students involved in this work, and to the Robert A. Welch Foundation for support of the research program from which came the idea for this experiment.

errors are almost certain and really good results are seldom achieved in the time which can be allotted. Furthermore, time for instruction and practice in the adaptation and use of the applicable instruments is often curtailed by the interval required for the preparation of the sample.

The experiment described here retains a minimum of objectionable features and has proved useful as a first experiment in turbidimetry. Even students in the introductory analytical course have had no difficulty achieving adequate results after proper introduction to the use of the optical instruments.

Molybdate Ion as Precipitant

As a means for the actual determination of lead, the method discussed here may perhaps have nothing in particular to recommend it. There are many excellent procedures in the literature for the analysis of lead and any new method would require that some special circumstance make it necessary. The method reported here, however, is not essentially new; for many years the molybdate ion has been used as a precipitating agent in the gravimetric determination of lead. A gravimetric procedure employing this reagent may be found in Scott's "Standard Methods of Chemical Analysis."[1] In Scott's procedure a troublesome suspension of lead molybdate is mentioned for which special precautions must be taken during washing to achieve a filterable precipitate. The turbidimetric method, which also utilizes the molybdate ion as precipitant, makes use of this otherwise troublesome suspension and becomes an alternative to the gravimetric method, replacing the filtration, ignition, and weighing required in that method. There is no doubt that, with scant modification, it could be put to use as a practical means of determining lead. That it has not been touched upon in the literature bespeaks both the unpopularity of the turbidimetric method and the wealth of optional analytical procedures. Nevertheless, with its close similarity to the gravimetric procedure and its obvious applicability, it need not be considered by the student as a method fabricated wholly for convenience as a laboratory experiment. This is important for the impartial presentation of turbidimetry as a valid means of analysis.

The Experiment

Standard lead solution. Dissolve 1.342 g of reagent-grade lead chloride in distilled water and dilute to one liter. This solution contains 1 mg of lead per ml.

Ammonium molybdate reagent. Dissolve 4 g of ammonium molybdate in distilled water, add 10 ml of glacial acetic acid, and dilute to one liter. This solution is identical to that used in Scott.[1]

Appropriate volumes of the lead solution are diluted to 25 ml to give a series of standard solutions of concentration, 10, 20 . . . 100 ppm lead. Samples to be analyzed are first diluted to give a concentration within the range of the standards and then 25 ml portions are taken for preparation of the turbidity. To each of these solutions, contained in a large test tube, a 5 ml sample of the reagent is added by introducing a 5 ml pipet gently to the bottom of the tube, allowing the solution to flow out under the influence of gravity until the liquid levels are almost equal, then gently removing the pipet and allowing the last portion to run in from just above the surface. When the pipet has been emptied, the tube is carefully stoppered and allowed to sit for fifteen minutes. At that time the contents are shaken and transferred to a suitable sample vessel for measurement by one of the following instrumental techniques.

Spectrophotometric Technique

It was found convenient to prepare permanent comparison standards for this technique:

Comparison standard A. Sufficient ammoniacal thymol-blue solution was added to distilled water to give the resulting mixture a transmittance of 70% when compared with water at 525 mμ using half-inch cells.

Comparison standard B. A second solution of thymol blue was adjusted to give 20% transmittance at 525 mμ when compared with water in half-inch cells.

These solutions were originally employed in place of a turbid standard in order to provide a constant basis of comparison for evaluating the reproducibility of various methods of precipitation. A reagent blank gave too high values of absorbence while the colored comparisons could be prepared with various transmittances and provided an equally permanent reference. Thymol blue was chosen for convenience. Other reference standards may be employed with equally good results.

Comparison standard *A* was used for the 10–50 ppm concentration range and comparison standard *B* for the 60–100 ppm range. A wavelength of 525 mμ was employed, half-inch cells were used to hold the solutions, and the sensitivity of the instrument was adjusted until the comparison standards gave 100% transmittance.

A typical working curve is in two parts and is shown in Figure 1. The results do not conform to Beer's law but the deviation is sufficiently slight to allow the construction of two straight-line segments of unequal slope. For the curves of Figure 1 the samples were maintained at constant temperature in order to evaluate

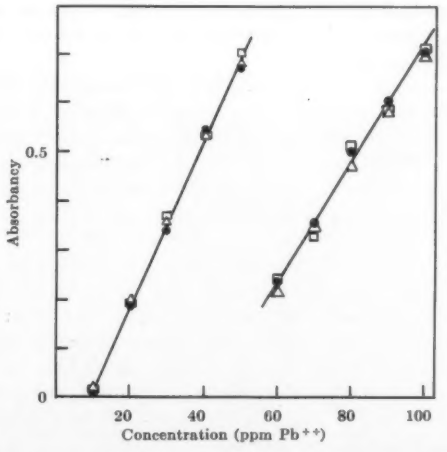


Figure 1. Two-part working curve obtained with the Bausch and Lomb Spectronic 20, using half-inch test tubes. 10–50 ppm vs comparison standard A; 60–100 ppm vs comparison standard B. (●, 20°C; □, 25°C; △, 30°C.)

[1] Scott, W. W., "Standard Methods of Chemical Analysis," D. Van Nostrand, New York, N. Y., 1947, Vol. 1, p. 506.

the influence of that variable. Points have been plotted for three temperatures in the interval, 20–30°C.

Colorimetric Technique

A suspension of lead molybdate produced from a 50 ppm concentration of lead was used as the comparison standard for the colorimetric work. Once again the deviation from Beer's law makes it necessary to construct a working curve. This may be done by plotting the ratio, depth of standard/depth of sample, as a function of concentration, since this type of curve allows the necessary flexibility in cup adjustment. The concentration of the standard should be about the same as the mid-concentration of the samples. A typical curve is shown in Figure 2. For convenience, the data are again fitted with two straight lines. All data obtained with the colorimeter were gathered at room temperature.

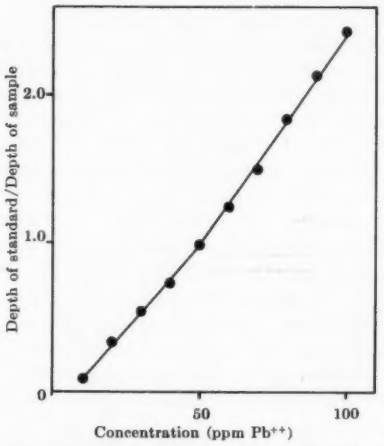


Figure 2. Working curve obtained with the Duboscq Colorimeter using a comparison standard of 50 ppm Pb.††

Student Results

The procedure was checked by students in both introductory instrumental analysis and elementary quantitative analysis courses. The latter group employed the Duboscq colorimeter while the more advanced class used the Bausch and Lomb, Spectronic 20, spectrophotometer.

The group working with the Spectronic 20, with the aid of curves similar to Figure 1, constructed from data obtained at room temperature, performed 26 analyses on samples of unknown composition, ranging from 12 to 94 ppm lead. These analyses were done at room temperature. The average error was 2.9% and the maximum error in any one analysis was 6.7%. The average error of the 13 samples covering the range 10–50 ppm lead was 4.2%; of the 13 samples covering the range 60–100 ppm lead, the average error was 1.6%.

The results of nine student analyses employing the Duboscq colorimeter are shown in Table 1. The average error for all trials was 3.6%, a value which would have been considerably reduced had some data been statistically rejected.

The student analyses reflect an accuracy which is as good as is normally expected for this type of measurement. Moreover, in the spectrophotometric analysis

Table 1. Student Analyses with the Duboscq Colorimeter

Pb added (ppm)	Pb found (ppm)	Error (%)	Pb added (ppm)	Pb found (ppm)	Error (%)
10	10.0	0.0	70	69.4	0.9
20	22.7	13.5	80	81.8	2.3
30	31.3	4.3	90	92.8	3.1
40	42.0	5.0	100	100.0	0.0
60	58.2	3.0	..	...	..

the true accuracy of the method could exceed that indicated by the student errors, for these may contain additional inaccuracies produced in diluting stock solutions to prepare the synthetic samples. This seems to be indicated by the larger error obtained for the 10–50 ppm range. The samples shown in Table 1 were taken from the solutions used to establish the working curve and their errors show no relationship to sample concentration.

The procedure utilizes an irreducible minimum of solutions and produces a stable, white suspension. No additives are needed and no special handling is involved in preparation of the reagent. The temperature need not be controlled unless it deviates markedly from 25°C. The concentration of the reagent may vary within wide limits. The value recommended for the reagent concentration was chosen because it accompanies a standard, published, gravimetric procedure[1] and will allow the use of this procedure as a guide to sample handling. The concentration of lead in the sample should fall approximately within the range 10–100 ppm. At concentrations somewhat less than this, the slope of the working curve obtained with cells of practical dimensions becomes too small for accuracy, and at concentrations somewhat above this range, the suspension settles out rapidly enough that time becomes a critical factor.

In the recommended procedure the only critical point occurs during the introduction of the precipitant. The system must remain unstirred at this time and the velocity of precipitation must not differ greatly from that afforded by the recommended slow addition of reagent. More rapid addition produces a colloidal suspension which fails to give reproducible results. Less rapid addition can be achieved only with added inconvenience. After addition of the reagent the system should remain unstirred for at least 10 minutes. The directions call for 15 and this allows a safety factor. After stirring, the solution may be kept for several hours without appreciably affecting the results. This gives ample time for measurement during a normal laboratory period. It must be held in mind, if the procedure in Scott is used for treating the sample, that the object of that procedure is a filterable precipitate, and an excess of ammonium nitrate helps to precipitate the suspension. Consequently, the quantity of ammonium nitrate produced in his treatment must be either held to a minimum or partially dissipated by evaporation for adaption to the experiment here described. Certain other salts also tend to precipitate this suspension and for application of this method to special samples, it is suggested that Weiser's study of this precipitate[2] be consulted.

[2] WEISER, H. B., *J. Phys. Chem.*, **20**, 640 (1916).

William F. Head, Jr.[1]
and **Max M. Marsh**
Eli Lilly and Company
Indianapolis, Indiana

An Inexpensive Coulometer for Titrations with Externally Generated Reagents

Most commercial coulometers consist of a highly regulated direct current power supply, to insure a constant current, and an apparatus for accurately timing the duration of the electrolysis, usually an integral electric stopwatch. This technique is particularly useful for the internal generation of reactants. Coulometers have also been designed to operate at controlled potentials, allowing the current to decrease exponentially with time. This method of operation is widely used, especially when the material to be analyzed is subject to direct electrolytic action.

Description of the Coulometer

The circuit diagram of the instrument is shown in Figure 1.[2] Figure 2 is a photograph of the assembled circuit and a special buret designed for separation of anode and cathode products in a flowing electrolyte. The dc power supply designed for use with this equipment is conventional. The 110-volt ac line current is passed through a variable transformer and through a full wave selenium rectifier. The output of the rectifier used with a 1000-mfd condenser gives direct current of reasonably small ripple fluctuation; if desired, a choke could be placed in series at this point to further reduce ripple. The dc output is passed through a 500-ohm variable resistor. The electrolysis cell is connected in series with the variable arm of this resistor, thus allowing the desired cell voltage and current to be selected. The cell current is passed in series through an ammeter (to estimate titrant generating rate), the cell, and a variable 50-ohm resistor. A voltmeter is used to obtain approximate cell voltage drop.

For measurement of the quantity of electricity passed through the cell, a special low inertia motor, the speed of which is directly proportional to the voltage applied to its terminals, has been used.[3] This has been done to facilitate direct readout, rather than using calculations involving time of current flow. In addition, electronic feed-back facilities have not been designed into the instrument so that neither current nor potential is absolutely constant. The motor terminals are connected across the 50-ohm variable resistor which has been tightened into one position for maximum sensitivity. The value of the resistance cannot be changed without going into the instrument case. If this value is changed, the calibration factor or motor sensitivity to cell current will change. It can be considered as a fixed resistor of optimum value. The current passing through the cell must also pass through this resistor, thereby producing a voltage drop; this voltage is "sensed" by the motor. If the current flowing through

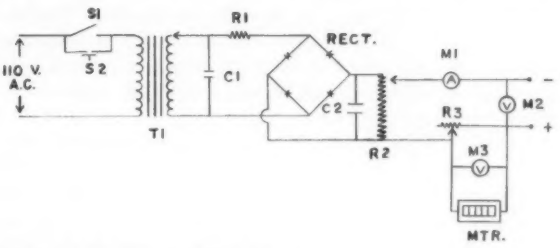


Figure 1. Coulometer circuit diagram.

S1	On-off switch	*R2*	500 ohms, 150 w, Ohmite No. 0541
S2	Momentary contact switch	*R3*	50 ohms, 10 w
T1	Powerstat Type 20, 3 amp	*M1*	0–1 amp
C1	0.05 mfd, Aerovox P-88, 600 v	*M2*	0–100 v dc
R1	45 ohms, 10 w	*M3*	0–8 v dc
C2	1000 mfd, 150 v dc, P.R. Mallory		

RECT.—Selenium rectifier, 2.0 amp output, maximum ac input 156 v, maximum dc output 120 v.
MTR.—Current integrating, low-inertia motor, Electro Methods Ltd., Stevenage, Herts, England.

the cell changes, the voltage across the measuring resistor changes accordingly, thereby either increasing or decreasing the motor revolutions. A lightweight, mechanical, counter unit is geared to the motor shaft so that after a period of electrolysis, a number of counts is registered. The counter unit cannot be reset to zero; subsequent determinations must be made by

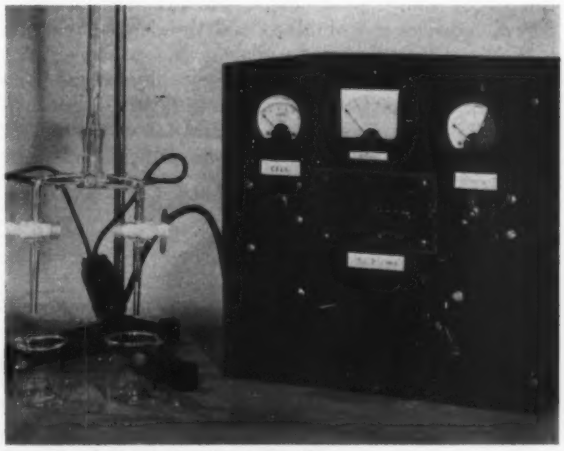


Figure 2. Coulometer and buret assembly.

[1] Present address, School of Pharmacy, Auburn University, Auburn, Alabama.

[2] The authors are indebted to Mr. Harold Plummer for assembling the final circuit.

[3] Lingane, J. J., *Anal. Chim. Acta*, **18**, 349 (1958).

subtracting counts before electrolysis from counts after electrolysis.

Description of the Buret

In 1951, DeFord, Pitts, and Johns[4] described a buret having two outlet tips. In each outlet arm of the buret was placed a platinum spiral which served as one electrode of an electrolysis cell. When the spirals were connected to a direct current source and electrolyte allowed to flow simultaneously through both arms of the buret, products of the anode and cathode were effectively separated, removed from the electrode area, and delivered into separate containers while fresh electrolyte flowing from an electrolyte reservoir continued the process. This provided a very convenient means of performing coulometric titrations using externally generated titrants, thus eliminating interferences, secondary reactions at electrodes, etc., when titrant was generated internally. It also allows the simultaneous generation of acid and base or oxidizing and reducing agents which could not be done internally if the products were diffusable since they would react with each other, as well as with the test material.

This buret, as described, has been constructed with only slight modifications and gives excellent performance. The platinum spirals were replaced with platinum gauze rolled into cylinders and recessed in standard taper male joints. The buret was made with small standard taper joints to facilitate dismantling and cleaning. At points on the anode and cathode delivery tips, beyond the electrodes, Teflon stopcocks were inserted to provide a means of controlling the flow rate of generated titrant. There are no milliliter markings on this buret, since the actual measurement of titrant delivered is made coulometrically.

Use of the Instrument

The coulometer has been calibrated in terms of *counts per milliequivalent* using a silver deposition method. During this calibration, the instrument has been used as a standard coulometer (without the buret assembly). This is one method of operation, although no accurate voltage controls exist for precise selection of electrode reactions. The leads to the buret are disconnected and attached to the standard coulometric cell being employed. As in all coulometric work of this type, conditions must be selected so that 100% current efficiency is obtained and the desired reaction is the only reaction taking place. End points are not detected by this instrument. They may be detected by standard methods such as indicators, potentiometers, amperometers, etc., and the coulometer turned off manually. There has appeared in the literature[5] a description of a coulometer which was coupled to a Beckman Automatic Titrator, Model K, for completely automatic titrations. This apparatus could be added to the coulometer if desired.

The buret assembly has been used with the coulometer for generation of sodium hydroxide and sulfuric acid from an approximately 1 *M* sodium sulfate electrolyte. Titrations performed with these reagents are within 0.2 count per milliequivalent compared to the silver deposition method or within 0.38%. Other electrolytes could be used but they should be neutral in solution for acid-base titration; if not, the excess electrolyte not converted to titrant will affect the end point. Iodine can be easily generated at the anode using a potassium iodide electrolyte. When titrations are performed, both buret tips must be opened and the undesired electrode product collected in a waste beaker.

Some non-aqueous titrants may also be generated quantitatively using the same instrument calibration. Lithium methoxide was generated using a lithium chloride solution in methanol. "Super-dry" methanol and anhydrous lithium chloride excluded the possibility of lithium hydroxide formation. It was found, however, that absolute methanol and reagent lithium chloride worked equally well in the titration of benzoic acid in dimethylformamide. There is some moisture in this system but not enough to interfere. Since the resistance of the non-aqueous electrolytes is higher than the aqueous media, somewhat higher cell voltages are necessary to obtain a convenient generation rate.

Mather and Anson[6] have given a recent summary of the problems involved in acidimetric titrations in non-aqueous media. An entirely non-aqueous media was devised for the electrochemical generation of hydrogen ion utilizing the oxidation of a mercury electrode and subsequent reaction with acetate ion. Unfortunately, with a platinum electrode, this system will not function. The acetonitrile-water-hydroquinone system, described by Hanselman and Streuli,[7] will perform satisfactorily since it depends on the oxidation of water and hydroquinone to produce hydrogen ion. A solution of 240 mg hydroquinone and 14 g sodium perchlorate monohydrate in a liter of acetonitrile containing 0.4% water was found to give generation rates of about one-third that possible with aqueous 1 *M* sodium sulfate. Amines in glacial acetic acid have been readily titrated using this method of external generation of essentially non-aqueous protons.

[4] DeFord, D. D., Pitts, J. N., and Johns, C. J., *Anal. Chem.*, **23**, 938 (1951).

[5] Sundberg, O. E., Craig, H. C., and Parsons, J. S., *Anal. Chem.*, **30**, 1842 (1958).

[6] Mather, W. B., Jr., and Anson, F. C., *Anal. Chim. Acta*, **21**, 468 (1959).

[7] Hanselman, R. B., and Streuli, C. A., *Anal. Chem.*, **28**, 918 (1956).

Who Am I?

Leucine Phenylalanine-Serine
or Leu Phe·Ser (pronounce it!)

(*See page 352*)

Howard M. Myers
University of California
Medical Center
San Francisco

Revised Teaching of Biochemistry

The teaching of biochemistry in professional schools is difficult. While those familiar with the subject do not doubt its value, the recipients of the course remain unconvinced of its merit. Thus, teachers of this subject must overcome poor motivation as well as the more ordinary problems of communication and pedagogy.

The motivation problem is compounded by the subject matter itself: much detail, great quantities of preparatory material, and elaborate terminology all increase the difficulties of a poorly motivated student.

The ultimate objective of teaching biochemistry is to develop an ability to use biochemical principles and information in new situations. The catalogue of phenomena which have biochemical components is limited only by a knowledge of biochemistry which can be readily mobilized. Many applications, admittedly, are never made; this is probably the result of disillusionment on the part of the student who, after attempting a few enthusiastic but feeble biochemical attacks on problems, succumbs to the mode of life in which questions of non-routine nature seldom arise. To promote the use of biochemistry in solving technical problems, exposure to bigger courses of biochemistry is not enough. No mental discipline *per se* is developed in the study of biochemistry; the content and its significance in problem solving must be emphasized. In the conventional approach the applications of facts to specific problems are *assumed* to occur, with the result that only the most superior students are able to make such a transfer.

There are several fields where concepts developed in biochemistry may be expanded further. These include pathology, genetics, nutrition, bacteriology, and pharmacology, with several specific examples in each discipline of the application of a biochemical idea. In addition to the specific preparatory value of biochemistry in these instances, the student will gain a great advantage if he learns the pattern of thinking that leads to the application of acquired facts to a new situation. It appears to this writer that the chief objective of a professional school biochemistry course is to develop those patterns of thinking which facilitate such applications. This skill should be deliberately taught and emphasized along with the factual material.

At present biochemistry teaching is overburdened with the details of the preparatory organic and physical chemistry as well as of the intermediate metabolism on which biochemistry is built. The intent is for the details to be combined into an integrated understanding of biochemistry. As a rule, however, no meaningful integration of the material is accomplished, primarily because the arrangement of subject matter is rigorously logical. Enzymes, which are proteins, are studied after protein chemistry; carbohydrate and lipid chemistry precede carbohydrate and lipid metabolism. The result is highly logical but segmented subject-matter in which interrelationships are perceived late in the course if at all. It is understandable that motivation in such a course will be low, that insight into principles will be rare, and that transfer of facts into new situations will be exceptional rather than the rule.

A typical lecture sequence for biochemistry is to be found in the chapter headings of any standard text. This often has the effect of fractionating the subject, and with instructor and student alike losing sight of unifying principles. An unusual amount of insight by the student is required before anything lasting is taken from the course; this is seldom achieved, since most students become lost in a forest of details. The rapidly growing mass of detail in the field only adds to the confusion if new material is incorporated annually into the lecture material. It is ironic indeed that a course in which interrelationships are so important should result in disjointed understanding of the content.

Suggested Revision

The revision of the biochemistry course here suggested is based on a sound psychological sequence of topics rather than the traditional rigorously logical one.

The course is based on a fundamental concept of biochemistry. This concept has been chosen because it is familiar to everyone and can easily be understood, and because it serves as a link between past biological training and the material of the course. Simply stated, it is "energy is derived from the food we eat." The manner in which this energy is derived is a chief concern of biochemistry. The heat produced by the oxidation of food is largely useless for biological work such as tissue repair or muscle contraction. These latter functions are accomplished by a specially created compound called adenosine triphosphate (ATP). The synthesis of this compound is a fundamental consideration in metabolism. Foods are digested, absorbed, and metabolized in such a way as to promote the formation of ATP. Carbohydrates and lipids are converted to compounds which can readily yield energy in the form of ATP. The Krebs tricarboxylic acid cycle is the chief mechanism for making ATP from these compounds. Protein also can give rise to ATP by way of this cycle but must first have its nitrogen removed and eliminated in the form of urea. Vitamins play a role in converting the energy inherent in the oxidation of food into a biologically useful form, ATP.

As a result of the chemical reactions leading to the

manufacture of ATP, waste products like carbon dioxide and urea are formed. The elimination of such waste products without interference with the economy of the body becomes the second basic concept of the course; the homeostatic control of *p*H, isotonicity, etc., can be understood in relation to the derivation of ATP by oxidation of food.

Finally it remains to be shown how ATP releases its energy for such purposes as synthesis of tissue or for muscle contraction. The phenomena of tissue repair, fiber formation, and even calcification can thus be related to the fundamental process of building ATP and its cleavage to yield useful energy.

The outline proposed can include the same details that are by tradition being taught in a different sequence. The topics can be related easily to a few basic concepts which serve to unify them. The advantage of this arrangement over the traditional segmented pattern of topics should be obvious: while the same key concepts are present in the conventional biochemistry course, they are submerged in a mass of detail and do not enhance the learning process.

If the use of the proposed plan does improve mastery of the detail by ordering it into a more psychologically acceptable pattern, we must still consider methods for promoting the use of this information.

Illustrative Clinical Problems

It would seem that actual problems should be presented which can be analyzed into their biochemical components. The process of the analysis can be clarified by questions which lead into the mass of biochemical information possessed by the student. While the specific clinical problem discussed may be clarified, an even more fundamental advantage will ensue in that the pattern of analysis will be learned. This pattern can be subsequently applied to new problems as they arise. Since the writer has most of his teaching experience in a school of dentistry the examples which follow are applicable to this profession:

Question: What has salivary viscosity to do with retaining artificial full dentures? What components of saliva contribute to its viscosity? How may mouth conditions increase or decrease the viscosity of saliva? What kind of chemical reaction is involved in decreasing the viscosity of a secretion such as saliva?

Suggested Answers: A highly viscous liquid film between the denture and the tissue increases retention, since the force which must be applied to displace the denture increases directly as the viscosity. The polymeric mucins or glycoproteins are chiefly responsible for the viscosity of saliva. Increasing the rate of secretion of saliva by stimulation with drugs or chewing dry materials rapidly decreases salivary viscosity. Mucinases produced by oral bacteria cause a loss of viscosity in a matter of a few hours by depolymerizing the mucins. Sympathetic stimulation of the salivary glands produces thick viscous saliva while parasympathetic stimulation decreases salivary viscosity.

Question: The occurrence of rampant caries (decay) may be associated with medical case histories involving colitis. What may the relationship be due to? What is an important symptom of colitis? How does this symptom effect water balance? What effect does dehydration have on saliva production? How is "dry mouth" related to the incidence of dental decay?

Suggested Answers: The diarrhea of colitis leads to dehydration. Over 8000 ml of water could theoretically be lost via the G.I. tract in severe diarrhea while only 100 ml are normally lost by this route. Dehydration is a cause of dry mouth and the incidence of decay is consistently greater where salivary flow is reduced.

Question: What effect does a low *p*H have on the salt form of a local anesthetic? Why are areas of infection regarded as having a lower than normal *p*H? What is the effect of inadequate oxygenation due to stagnation of blood supply? What happens to carbohydrates metabolized in the absence of oxygen?

Suggested Answers: A low *p*H allows more of the anesthetic to exist as a quaternary salt. The anesthetic compounds must be converted to a free base to be effective. Inflammation involves stagnation of blood supply and subsequent inadequate oxygenation of the tissue. In the absence of oxygen lactic acid accumulates. In the presence of oxygen lactic acid is not accumulated but is converted to pyruvic acid which can be further metabolized in the tricarboxylic acid cycle.

The course revision discussed above in broad terms has the merit of unifying biochemistry around the concept of energy derivation from food. A more detailed topic outline is available from the author on request for those interested in pursuing this revision further.

With a clear view of objectives, the teaching method can be slanted toward these objectives in as direct a manner as possible. Teaching for application is to be continually stressed, and the intellectual pattern of making the application is to be reinforced by deliberate intent. Much elimination of meaningless detail can be accomplished by organizing the subject matter along the lines of unifying principles. When facts become subservient to ideas and concepts, they are more likely to be mobilized to help solve new problems than if they are allowed to obscure the field. Such is the rationale of the proposed changes in the teaching of biochemistry.

MCA Honors Six College Chemistry Teachers

The 1961 College Chemistry Teacher Awards of the Manufacturing Chemists' Association were made on June 8, 1961. The following medalists were chosen from 187 nominations submitted by college and university presidents:

Richard McLean Badger, California Institute of Technology, Pasadena
Ellis Llewellyn Krause, Marietta College, Marietta, Ohio
Samuel Proctor Massie, Jr., Fisk University, Nashville, Tennessee
Louis Abell Pappenhagen, Mount Union College, Alliance, Ohio
John R. Sampey, Jr., Furman University, Greenville, South Carolina
R. Nelson Smith, Pomona College, Claremont, California

Francis E. Crane, Jr.
Douglass College
Rutgers, The State University
New Brunswick, New Jersey

Is There an Alternative to *p*H?

Surprising as it may seem, there have been many unsuccessful attempts over the years to replace the *p*H concept. Most of these suggested substitutes are related to the hydrogen ion concentration $[H^+]$ in a more complicated manner than is *p*H itself. The reluctance of the scientific world to change from *p*H may be explained partly on that basis.

The introduction of *p*H as a function of $[H^+]$ by Sörensen in 1909 was a significant event in the history of chemistry. It eliminated the disagreeable task of working with very small decimals or with large negative exponential powers of ten when the $[H^+]$ is low, i.e., in weakly acid, neutral, or alkaline solutions. However, to some it may seem unfortunate that Sörensen defined his *p*H term as the negative logarithm of $[H^+]$. This definition requires that as a solution becomes more acidic, $[H^+]$ increases whereas *p*H decreases. *p*H appears to be related inversely to $[H^+]$ and when $[H^+]$ is greater than unity, the *p*H is actually negative. This situation is difficult for some beginning chemistry students to comprehend.

Some Alternative Proposals

Wherry and Adams (*1*) recommended in place of *p*H the use of a chemical potential term, X_H, defined as $7 - pH$, and a specific acidity scale, "*S.A.*," defined as $[H^+]$ times 10^7. Thus, when *p*H is less than 7 (in acidic solutions) X_H is always positive and increases in direct relation to $[H^+]$. Also, *S.A.* increases in direct relation to $[H^+]$ and is always greater than 1 in acid solutions. In neutral solutions, when $pH = 7$, $X_H = 0$ and $S.A. = 1$. Later, Wherry (*2*) changed his nomenclature for the *S.A.* scale to the "active acidity" scale, and introduced an "active alkalinity" term especially for basic solutions. This alkalinity term, "*A.A.*," was defined as equal to the hydroxyl ion concentration times 10^7. *A.A.* is equal to 1 at neutrality and becomes progressively more positive than 1 in alkaline solutions, whereas X_H becomes progressively more negative. Wherry claimed a major advantage to be that his computations begin at the neutral point.

Clark (*3*) raised several objections to Wherry's terms, chiefly that the X_H method involves an assumption, which is never used, regarding the nature of pure water; that X_H values are not directly derived from the potential of the normal hydrogen electrode; that the X_H scale does not have a sufficient advantage over *p*H to warrant a change; and that Wherry's specific acidity scale is unfamiliar and puzzling, and obscures those logarithmic relationships which are valuable for students.

Derrien and Fontés (*4*) proposed that acidity be expressed as the logarithm of $[H^+]$ in micro units per liter. This term *DF* actually amounts to $\log 10^7 [H^+]$ in mole per liter concentration units. As a solution becomes less acid, the positive value of *DF* decreases until it becomes zero at neutrality and progressively more negative as the solution becomes more alkaline. Another system, which claims the advantage of giving positive values for acidic solutions, zero for neutrality and negative values for alkaline solutions was described by Giribaldo (*5*). Instead of using $[H^+]$ to express acidity, the term $\log [H^+] - \log [OH^+] = \log H^+/OH^-$ or $\log r$ was advocated. Also $\log r$ equals $\log [H^+] - (\log K_w - \log [H^+])$ in water solution. This simplifies to $\log r = 2 \log [H^+] - \log K_w$.

Kolthoff (*6*) has commented at length on the methods which were proposed up to 1926 to replace the *p*H method. He states that it is confusing to attach a special meaning to neutrality in biological systems as Giribaldo and Wherry had done. Also, no special meaning should be given to a *p*H of 7, because only pure water has this value. Kolthoff concluded that Sörensen's *p*H should be retained, and none of the new methods adopted. Specific disadvantages of the Giribaldo system were mentioned: (1) the values of r change as the square rather than the first power of the change in $[H^+]$; and (2) the $\log r$ scale is different at each temperature due to the changing value of K_w. Later, Giribaldo (*7*) claimed that his new *pR* values do not vary with temperature, while the theoretical *p*H does, owing to the varying dissociation of water.

A unit of acidity named "hydron" was proposed by Gerstle (*8*). Because this unit is too large for practical purposes, he preferred the "decihydron" equal to $^1/_{10}$ of a hydron. The number of decihydrons, N_{dh}, in a solution $= 10 \log (a_{H+})_1/(a_{H+})_2$ where $(a_{H+})_1$ and $(a_{H+})_2$ represent respectively the hydrogen ion activity in the solution under investigation and that of the standard reference. As a practical standard of comparison, he suggested pure water at 22° C, in which $(a_{H+})_2 = \sqrt{K_w} = 10^{-7}$. Thus $N_{dh} = 70 + 10 \log (a_{H+})$. Advantages were claimed over the *p*H system: hydrogen ion activities have a more rational meaning; acidity and alkalinity are easily distinguishable by the plus and minus signs; the numerical extent of the range has been increased, without resorting to small decimal values; and the zero point corresponds to the hydrogen ion activity of pure neutral water at 22° only.

Miller (*9*) recommended that *p*H be expressed as an arithmetical quantity either as active acidity "A_H" or active alkalinity "A_{OH}." These terms were defined strictly on the basis of H^+ and OH^- ion concentrations. A table listing A_H and A_{OH} in familiar arithmetical and

equivalent logarithmic terms was given. Catani (*10*) believes that both the *p*H and *pR* systems are inadequate, and proposed an *rA* (meaning reaction actual) system to replace them. The *rA* value was expressed as milliequivalents of ionic hydrogen per liter, with alkaline solutions given negative values.

In 1952 Valentinuzzi and Lango (*11*) advanced additional reasons for adoption of Giribaldo's *pR* system. They claim that a constant numerical value of $pR = 0$ indicates neutrality independent of the temperature, and that the absolute value of *pR* is directly proportional to the deviation from neutrality. Also, several of the important formulas giving the *p*H of strong acids and bases, weak acids and bases, ampholytes, and buffer and salt solutions were changed into *pR* terms. Hitchcock (*12*) states that further work should be done to determine whether $-\log C_H f_H$ or $-C_H f_H^2$ is more useful than *p*H as a measure of acidity or alkalinity, and whether simpler methods can be found for measuring these quantities (*f* is the activity coefficient).

A Further Alternative

Virtually all of the previously mentioned acidity systems were designed to replace the conventional *p*H term. A "*c*H" term is another way of expressing the $[H^+]$ in a solution. This term is designed to supplement *p*H but not to replace it, and is defined as:

$$cH = \log [H^+] + 16 \qquad (1)$$

*c*H has the advantage that it has a direct rather than an inverse relation to $[H^+]$ and is always positive unless the solution becomes extremely alkaline, i.e., where the $[H^+]$ is less than 1×10^{-16} *M*. When the acidity decreases to a $[H^+]=10^{-16}$, then *c*H decreases to 0. The neutral midpoint of the scale is 9. Also, *c*H is no more dependent on temperature than *p*H.

$$\text{Since } cH = \log [H^+] + 16 \qquad (1)$$

$$\text{and } pH = -\log [H^+] \qquad (2)$$

$$\text{then } pH = 16 - cH \qquad (3)$$

It is simple to transform from *c*H to the conventional *p*H unit, if desired. Thus, the acidity concept can be introduced to the beginning student by means of the constant 16, which is easily remembered because it is the basis of the chemical atomic weight scale. Another suggested use of this teaching device may be as an exercise to clarify in the student's mind the various equations based on $[H^+]$ which are often expressed merely in terms of *p*H.

It will be noticed that equation (3) is reminiscent of the relationship between *p*H and *p*OH, which is equal to $-\log [OH^-]$. In water solutions of low ionic strength at 25°, $pH = 14 - pOH$. Thus:

$$cH = pOH + 2 \qquad (4)$$

The important equations in aqueous neutralization chemistry are usually expressed in terms of *p*H. These equations can be transformed readily into *c*H units. For example, in titrations of various acids with various bases, the equations applicable at the stoichiometric equivalence points would be as follows:

where $pH = {}^1/_2\, pK_W$
$cH = 16 - {}^1/_2\, pK_W = 9.00 \qquad (5)$

where $pH = {}^1/_2\,(pK_W - pK_b - \log [B^+])$
$cH = 16 - {}^1/_2\,(pK_W - pK_b - \log [B^+]) \qquad (6)$

where $pH = {}^1/_2\,(pK_W + pK_a + \log [A^-])$
$cH = 16 - {}^1/_2\,(pK_W + pK_a + \log [A^-]) \qquad (7)$

In buffer mixtures of weak electrolytes, HA, and their salts, A^-,

$$cH = 16 - pK_i + \log [HA] - \log [A^-] \qquad (8)$$

For titrations of weak diprotic acids, H_2A, by strong bases, if it is assumed that $K_1 + HA^- \cong HA^-$ and that $(H_2A) \cong (A^{-2})$, at the first equivalence point the approximate equation would be

$$cH = 16 - {}^1/_2\,(pK_1 + pK_2) \qquad (9)$$

At the second equivalence point, if it is assumed that $[A^{-2}] - [OH^-] \cong [A^{-2}]$, the approximate equation would be

$$cH = 16 - {}^1/_2\,(pK_W + pK_2 + \log [A^{-2}]) \qquad (10)$$

Corresponding electrochemical equations also can incorporate the *c*H term in place of *p*H. For example, when hydrogen and calomel electrodes are used, the pertinent equation would be

$$E = -E_r + 0.059\,(16 - cH) \qquad (11)$$
$$\text{or } E = 0.0944 - E_r - 0.059\,cH \qquad (12)$$

When a glass electrode, whose potential is 0.655 volt, and a calomel electrode are employed, the measured potential is

$$E = 0.655 + E_r - 0.059\,(16 - cH) \qquad (13)$$
$$\text{or } E = E_r - 0.289 + 0.059\,cH \qquad (14)$$

In the case of quinhydrone and calomel electrodes a similar expression results:

$$E = \text{constant} + 0.059\,cH \qquad (15)$$

Acknowledgment

We are indebted to the Rutgers University Research Council for financial assistance, which made this work possible. Also, thanks are due Professor Frank H. McGar for a stimulating discussion, and the Misses Maryellen Marrow and Ethel Regenberg for assistance in searching the literature.

Literature Cited

(1) Wherry, E. T., and Adams, E. Q., *J. Wash. Acad. Sci.*, **11**, 198 (1921).
(2) Wherry, E. T., *Bull. Wagner Free Inst. Sci.*, **2**, 59 (1927).
(3) Clark, W. M., *J. Wash. Acad. Sci.*, **11**, 199 (1921).
(4) Derrien, E., and Fontés, G., *Compt. Rend. Soc. Biol.*, **92**, 503 (1925).
(5) Giribaldo, D., *An. Soc. españ. fis. qúim.*, **22**, 555 (1924).
(6) Kolthoff, I. M., *Biochem. Z.*, **169**, 490 (1926).
(7) Giribaldo, D., *An. fac. qúim. farm.* (Montevideo), **2**, 3 (1938).
(8) Gerstle, J., *Trans. Electrochem. Soc.*, **73**, 9 (1938).
(9) Miller, L. B., *Paper Trade J.*, **109**, 22 (1939).
(10) Catani, R. A., *Rev. Brasil. qúim.* **15**, 264 (1943).
(11) Valentinuzzi, M., and Lango, R., *Rev. Otto-Krause*, **4**, No. 16, 86 (1952).
(12) Hitchcock, D. I., *Natl. Bur. Stand. Circ. No.* **524**, 205 (1953).

Robert D. Macomber
Pacific High School
San Bernardino, California

Chemistry Accidents in High School

The purpose of this study was to determine the frequency of chemistry laboratory accidents in secondary schools and to identify some of the factors associated with the cause of the most serious ones. The data is derived from questionnaires received at random from 148 public high schools in California.

As defined in the study, serious accidents are those in which there is loss of school time of more than a day as a result of injury, or permanent disfigurement. Moderately serious accidents are those requiring more than minor first aid treatment but not causing permanent injury or loss of more than a day of school time. Minor accidents are those that can be adequately cared for by minor first aid treatment.

The frequency of accidents was figured from 81 of the questionnaires; these included a listing of the total number of serious accidents and the enrollment in chemistry classes for the three school years from fall 1955 to spring 1958. They listed 13 individual serious accidents and 137 moderately serious for an average of 50 per year. Student enrollment in chemistry classes was 9123 per year in the 81 schools, a mean enrollment of about 113 students per school per year. There was one moderately serious or serious accident for every 182.4 students per school year in the sample studied or 0.61 accidents per school per year. Minor accidents are considerably more numerous.

The data in the remainder of this study was given by the chemistry teachers concerning the most serious accident in the laboratory in each school during the three year period. In Table 1 the accidents have been grouped into six types. Explosions and phosphorus burns contributed the largest percentage of serious though there were only three of the latter. Over 80% of the explosions reported resulted in moderately serious or serious injuries. The types reported include explosions of organic substances (2) and of gas generators (5), and explosions resulting from the mixing of potassium chlorate with combustible materials (5), and from the heating of sealed glass tubes containing liquid (2). One implosion was reported from vacuum in an ammonia fountain prepared from an Erlenmeyer flask rather than a round bottom flask.

Table 1. Distribution of 148 Laboratory Accidents by Type and Relative Seriousness

Type of accident	Number	Per cent	Per cent of the number of each type of accident		
			Minor	Moderate	Serious
Burn (heat)	44	26.2	79.8	20.2	0.0
Burn (acid or caustic)	28	16.7	28.4	68.0	3.6
Explosion[a]	15	8.9	13.3	53.4	33.3
Cuts	76	45.0	77.6	22.4	0.0
Poisoning	2	1.2	50.0	50.0	0.0
Phosphorus	3	1.8	0.0	33.3	66.6

[a] Includes one implosion.

The questionnaire attempted to determine several factors relating to the type of laboratory work in which accidents occur. These include size of laboratory section per instructor, whether the experiments were from published laboratory manuals, and actual student activity at the time of the accident. Table 2 shows that the accident hazards increase as the size of the laboratory section increases. However only one respondent reported class size of less than ten students so the data for this group is not meaningful.

Table 2. Distribution of 140 Laboratory Accidents by Seriousness and Class Size Per Instructor

Class size	Number	Per cent of total	Per cent of the number of accidents in each lab. size		
			Minor	Moderate	Serious
Under 10	1	0.7	100	0.0	0.0
11 to 20	9	6.4	77.8	22.2	0.0
21 to 30	95	67.9	60.0	37.9	2.1
Over 30	35	25.0	42.9	40.0	17.1

Accidents were still found to occur in schools using standard laboratory manuals. Nearly two-thirds of these were minor and were of the type in which the poor laboratory technique was responsible rather than any hazard present in the directions. Experiments prepared by the teacher or student did not show this same factor of safety (Table 3). This seems especially significant when project work is being so widely advocated in secondary school science.

Included in Table 3 were experiments being performed outside of school by students but with the teachers' knowledge. Though this figure is not compared with any number of successful experiments outside of school, within the limits of the available information it would seem that such experimentation is unwise.

Table 3. Preparation of Laboratory Experiments Related to Seriousness in 103 Accidents

Preparation of experiments	Number	Per cent	Per cent of the number of accidents for each type of preparation		
			Minor	Moderate	Serious
Published manuals	75	73.0	62.7	34.7	2.6
Teacher prepared	15	14.5	40.0	53.4	6.6
Student prep in school	8	7.7	37.5	37.5	25.0
Student prep out of school[a]	5	4.8	0.0	40.0	60.0

[a] Being performed outside of school but with the teachers' knowledge.

Table 4. Actual Student Activity at Time of Accident Related to Seriousness of Accident

Student activity	Number	Per cent of total	Per cent of the number of accidents for each type of student activity		
			Minor	Moderate	Serious
Following directions	77	70.5	59.7	39.0	1.3
On own seriously	21	19.3	33.3	52.4	14.3
"Horse play"	11	10.2	18.2	54.5	27.3

Table 5. Student's Achievement in Chemistry Compared with Seriousness of 126 Accidents

Accident seriousness	Number	Per cent of total	Per cent of the number of each category of seriousness		
			A–B student	C student	D–F student
Serious	8	6.3	62.5	0.0	37.5
Moderate	65	51.6	49.2	40.0	10.8
Minor	53	42.1	24.5	58.5	17.0

It can be assumed that few teachers would allow students to remain in chemistry classes if they continued to play around in the laboratory rather than do serious work. For this reason the number of accidents in Table 4 where "horse play" is involved was only 10% of the total. From the data available however, it would seem that the danger of injury is greater under this circumstance than when students are doing serious work. Of the accidents where "horse play" was involved, three of the students had previously been reprimanded for unsafe conduct. In four cases the teacher had some feeling that the student was an accident hazard, but the students involved in the remaining accidents were not considered to be in this category.

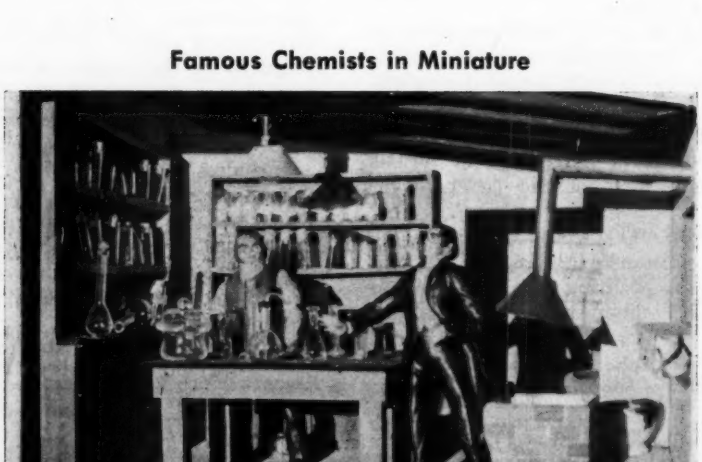
The tabulated factors concerning the type of student involved in the accidents reflect his achievement in chemistry and his scientific inquisitiveness as measured by teacher opinion. If only the serious and moderately serious accidents are considered, 40% occurred with students above average in scientific inquisitiveness. Nearly half of the students involved were average in inquisitiveness and only 11.5% were below average. Table 5 shows that the pattern of accidents compared to the students' achievement in chemistry correlates with the above data. Average students were involved in 45.5% of the cases and the D-F students accounted for only 15.2% of the total on the 126 questionnaires where this section was completed.

A follow-up letter to some of the teachers polled in this study brought out one significant item. Several said they finished their college chemistry courses with only vague ideas about the dangers involved in certain experiments or in the use of certain chemicals. Another teacher, with an envious injury-free record, allows students to do laboratory work only after they have made a perfect score on an extensive safety examination which has been thoroughly studied in class. This seems an excellent idea and one to be highly recommended.

Conclusion

Accidents are most likely to occur with the capable, inquisitive student, allowed to use his initiative while the teacher supervises others. The stage is set by large laboratory sections, and perhaps by too easy availability of a few substances that may not be essential for maximum learning.

Famous Chemists in Miniature



Mr. I. Q. Guillermo Romero of the Instituto Technologico y de Estudios Superiores de Monterrey sends this photograph of one of seven miniatures made for a Science Week display. A three-inch high Berzelius is calling on Sir Humphrey Davy. All glassware is actually blown to scale. Wood, paste, and cardboard are the other materials. The careful attention to detail includes facial characteristics and style of glassware appropriate to the period.

. . . from the CHAIRMAN

JOHN F. BAXTER

It is difficult to decide whether to address these comments to readers of THIS JOURNAL or to members of the Division of Chemical Education. It is obvious that they are not the same people. Subscriptions to the JOURNAL are now about 13,400 but membership in the Division is only about one-sixth of this figure, or a little over 2,000. Furthermore, not all members of the Division subscribe to the JOURNAL. All of you who do subscribe to and read the JOURNAL surely do so with both pleasure and profit. Since it is the official publication of the Division you can also take especial pride in the JOURNAL by joining with the Division as either Members or Associates, for then it will be *your* JOURNAL.

Those of you who are members of the ACS know that the Division of Chemical Education is one of 22 Divisions of the parent Society. Perhaps you did not realize that this Division probably cuts across a wider range of interests than any other. You who are not members of the ACS may not know that you can join the Division as an Associate and participate in all its activities except voting and holding office. Most of you who subscribe to the JOURNAL are eligible to join the Division and are indeed urged to do so. If you are interested in the object of the Division, "to afford a meeting ground for teachers and students of chemistry, as well as others who are interested in the larger aspects of chemical education, which include the training of professional chemists and indeed all the processes by which original knowledge and investigations are made understandable and usable to others" please reinforce this interest by sending your name and address and dues ($1.50 members, $2.00 associates) to W. G. Kessel, Treasurer, Indiana State, Terre Haute, Indiana. Let me repeat, you don't have to be an ACS member, you simply need to care about chemical education and your eligibility is assured.

As I write this, the St. Louis meeting is recently over. Your Division along with the 21 others sponsored all of the program except for the General Meeting. We had three full days of program including symposia on Recent Advances in the Chemistry of Fused Salts, Institutes and Conferences, and Audio-Visual Aids in Chemical Education. One full day was devoted to general papers. Nearly 200 attended the Divisional Dinner at Washington University to honor Dr. John C. Bailar, Jr., this year's recipient of the Scientific Apparatus Manufacturer's Association Award in Chemical Education. Dr. Bailar, who was Chairman of the Division in 1946–47, gave as his award address a penetrating look at "Chemical Education—Then and Now." You might like to know that a dinner meeting is planned for most National Meetings. It is usually held at a college in the area of the meeting so that prices can be kept as low as possible in pleasant surroundings. If you know that a National Meeting will be in your area soon and you would like to host a Divisional Dinner, communicate with the Chairman of the Program Committee. (We can't accept all invitations, of course, but it's nice to know we're wanted!) For the Chicago Meeting, Sept. 3–8, there will be symposia on the Teaching of Colloid and Surface Chemistry, Honors Programs in Chemistry, and Current Theories of Chemical Bonding. General papers will round out a balanced program. We are making an earnest effort to get out the meeting announcement "flyer" a month ahead of the dead-line for papers so that members can get their papers to the Program Committee Chairman on time.

I wish I could convey to you some of the sense of excitement which pervaded the various committee meetings in St. Louis. All eight of the members of the Executive Committee attended their meeting which lasted all day Saturday. Much of the business conducted was of a routine but necessary nature. One item under intense discussion was that of Teacher Associates. The ACS Council Committee on Chemical Education has been considering this problem for some time. An ad hoc committee for the Division consisting of Robert Silber, William Kessel, and Robert Maybury is to report to the Executive Committee in Chicago with recommendations for action at that meeting. The Sunday meetings of standing committees are always full of vigorous discussion and positive action, and the St. Louis sessions were unusually stimulating. Dr. H. Behrens of the University of Santiago in Chile, now visiting this country, was invited to attend the committee meetings. Much of the discussion centered around possible assistance to chemistry teachers and students in foreign countries where library holdings and general chemistry apparatus are minimal. An ad hoc Committee for Cooperation with Foreign Universities, just getting under way, met for the first time in St. Louis.

With the thought that Division Members and Associates might like to find out first hand what is going on, we are planning an Open Meeting at Chicago to be held jointly by the Committee on Teaching and the Committee on Institutes and Conferences, probably on Sunday afternoon, Sept. 3, at 2:00 PM. Meeting place cannot be announced at this time but if we find no convenient way to get this information to you in advance, it can always be obtained from the National Meetings Operations office after arrival in Chicago. You are all invited to this Open Meeting. Dr. William Cook, Secretary of the Division, prepared an Annual Report for 1960 for the Council Policy Committee. If you would like to see one of these, write to him and request one. Members now have the 1961 Directory of the Division and can find addresses there for all members, and a summary of much Division activity.

I trust you will agree with me that our Division is an active and thriving one. Once more I would like to appeal to all of you who are interested in chemical education, not now members, to join with us and lend your support to the work of the Division. Members, send your ideas to any of your officers or bring them with you to the Open Meeting in Chicago.

Proceedings of the

California Association of Chemistry Teachers

Curtis R. Joiner
U. S. Food and Drug Administration
Los Angeles, California

Pesticide Residue Control Under the Food, Drug, and Cosmetic Act

Insects have been a pest to man since prehistoric times, but they were never the serious problem they are today. The progress of civilization upset the balance of nature in many ways and resulted in the increase and spread of insects and other pests. Today it would be almost impossible to produce an adequate world supply of food without using pesticide chemicals.

The first organic insecticide probably was a crude extract of tobacco, which was used about 250 years ago to control the pear lacebug (*1*). Published recommendations for the use of arsenic trioxide as an insecticide date as far back as 1681 (*2*), and arsenicals probably were used long before that time. Before World War II the principal inorganic insecticides in extensive use were cryolite and the arsenicals; nicotine, rotenone, and pyrethrum were virtually the only organics. While most of these are still in use, they have been largely supplanted by new organic insecticides. More than 100,000 organic chemicals have been tested for insecticidal action, and over 100 are in commercial use.

Federal Laws Controlling Pesticides in Foods

As far as the control of pesticides in food is concerned, the Food and Drugs Act of 1906 prohibited "any added poisonous or other added deleterious ingredient which may render such article injurious to health." The Food, Drug, and Cosmetic Act of 1938 prohibited the addition of any amount of a poisonous or deleterious substance to food except where such substance was required in the production of the food or could not be avoided by good manufacturing practices. In the latter instances the Secretary was authorized to promulgate regulations limiting the quantities of such substances as necessary to protect the public health. Since pesticide chemicals were considered essential for the production of food, safe residues were permitted. The administrative procedures required by law for the setting of tolerances were so cumbersome and time consuming that only one formal tolerance was established between 1938 and 1954. Informal tolerances for lead, arsenic, and fluorine compounds were announced under the Food and Drugs Act of 1906 and were continued under the Act of 1938.

In 1954 the Congress enacted the Miller Pesticide Amendment to the Food, Drug, and Cosmetic Act. This amendment provides a simplified procedure for setting safe tolerances for residues of pesticide chemicals in raw agricultural products and for the establishment of exemptions from the necessity for tolerances when such are not needed to protect the public health.

The Federal Government's control over pesticides as such is vested in the U. S. Department of Agriculture (USDA) under the Federal Insecticide, Fungicide, and Rodenticide Act. Any individual or firm wishing to market a new chemical for use on a food crop, or extend the use of an old chemical to a new crop, must obtain a new registration of the labeling from USDA. If there is clearly no residue remaining on the food from such use, the Food and Drug Administration (FDA) is not involved in the registration of the chemical by USDA. If the proposed use of the pesticide chemical results in a residue on the crop at the time it is harvested, the complete experimental data must be submitted to FDA in the form of a petition for a tolerance for the chemical on that crop. The petition must include the data pertaining to the use of the chemical and the residues remaining on the crop at time of harvest, methods of analysis, and the results of pharmacological studies on the toxicity of the residues. USDA certifies that the chemical is useful for the intended purpose.

In considering petitions for tolerances, several factors are taken into consideration by FDA. The residue left on the crop by adequate application of the pesticide during the growing season must have been proven to be safe for consumption over long periods of time. If the data show that the residue is smaller than the maximum safe level, then the lower level is usually set as the legal tolerance. This policy affords an extra margin of safety for the consumer.

A specific tolerance must be issued for each crop on which the chemical is to be used. Over 2000 tolerances or exemptions from the necessity for a tolerance have been established for more than 100 pesticide chemicals. On apples, for example, there are tolerances for 48 different pesticide residues; on lettuce, 24; and on most crops of importance tolerances have been fixed for several different residues. Table 1 lists the tolerances that are effective for several commonly used pesticides.

Problems in Analytical Control

Many analytical problems remain to be solved in spite of the fact that requests for tolerances must contain a description of the analytical methods used for determining residues remaining on the crop. The

Based on a paper presented at the fall meeting of the Southern Section of CACT, Occidental College, Los Angeles, October 1960.

Table 1. Tolerances for Some Commonly Used Pesticides

Pesticides	Tolerances (ppm)	Food commodities[a]				
		Fruit and vegetables	Nuts	Grains	Animal products	Hay and forage
DDT	7.00	61	1	0	3	0
	3.50	1	0	0	0	0
Methoxychlor	14.00	45	1	1		
	100.00					6
BHC	5.00	42				
Heptachlor[b]	0.00	22	1	6		4
Aldrin	0.25	38	1			
	0.10	24		5		
	0.00	6		2		9
Dieldrin	0.25	31				
	0.10	22		5		
	0.00	11		2		8
Endrin	0.00	9				1
Parathion	1.00	61	1	4		5
Malathion	8.00	74	3	7		8
	4.00				5	
	2.00	2				
	0.00				2	

[a] Occasional changes cause these figures to vary.
[b] Includes heptachlor epoxide.

methods are not always practicable for routine control work, and interferences are frequently encountered. In analyzing samples for regulatory purposes, consideration must be given to possible interferences from all other pesticides for which legal tolerances have been established for that particular crop and also from some pesticides for which no tolerances have been set.

The extraction of the pesticide residue from the food crop is not always a simple matter. Some pesticides are absorbed by the plant and distributed systemically throughout the tissues; others remain entirely on the surface of the plant. Systemic insecticides must be extracted by blending the sample intimately with the solvent. Even nonsystemic insecticides are difficult to extract from the surface of leafy vegetables; for complete extraction these also must be blended with the solvent.

The sample extract can be used directly for a few determinations. Usually, however, it must be purified, or "cleaned up," before it is used. The extent of the clean-up necessary varies with the determination. More pigments, waxes, and other interferences are extracted by blending than by surface washing of the sample, and these are quite difficult to separate completely from the pesticide. The degree of clean-up required may be dependent upon the tolerance level of the pesticide being determined. For example, usually a larger sample will be required for one with a small tolerance of less than 1 ppm than for one with a tolerance of 7 ppm. It follows that the larger the sample needed for the determination, the more critical is the degree of purification required.

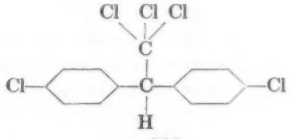
Extracts are frequently purified by passing them through columns of one or more adsorbents, such as Florisil®, Celite-sulfuric acid, magnesia (*3*), or alumina (*4*). Extraction with acetonitrile is useful for purification, alone or in conjunction with adsorbents. For volatile pesticides, a short path-high vacuum volatilization and condensation has been proposed as an additional purification step (*4*).

Legal actions against foods containing pesticide residues exceeding the established tolerances must be based on analytical results obtained by methods that are known to be reliable and specific for the particular pesticide chemical. This does not preclude, however, the use of rapid sorting methods to eliminate those samples that contain residues below the tolerances. The sorting methods usually are applied for groups of pesticides having structural similarities. The longer, specific methods need be used only for those samples shown by the sorting method to contain residues above or near the tolerance levels.

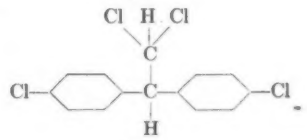
Chlorinated Hydrocarbon Pesticides

DDT and Related Compounds. The popular name, DDT, was derived from the generic name, dichlorodiphenyltrichloroethane; the chemical name for this compound is 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane. Zeidler in 1874 first synthesized and described the substance now known as DDT (*5*). The new compound was reported by him and forgotten. In 1939 a group of Swiss workers looking for mothproofing compounds resynthesized DDT (*5*). After extensive testing in the United States, pilot plant production of DDT was started in May 1943. Now more than 100,000,000 pounds are produced annually.

The phenomenal success of DDT led to the synthesis and testing of hundreds of compounds of similar structure. A few of these are in general use. TDE (from tetrachlorodiphenylethane) differs from DDT by one chlorine atom on the ethane moiety. This compound is less toxic than DDT to warm-blooded animals and to many insects. It is effective against certain insects, however, that are not controlled by DDT. Methoxy-

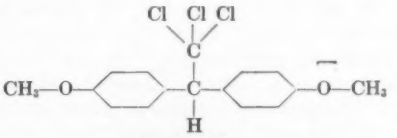


p,p' DDT



TDE

chlor, or 1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)-ethane, is useful against many insects and also has the advantage of being less toxic to warm-blooded animals than DDT. Both DDT and TDE are readily stored in the fat of animals if ingested, but methoxychlor is not appreciably stored.



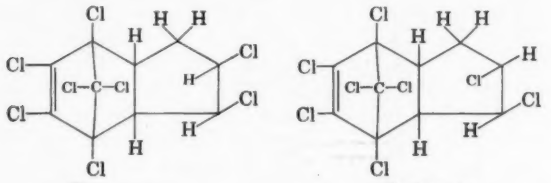
Methoxychlor

DDT, the first synthetic organic insecticide to be used extensively, is still probably the most common one in commercial use today. More violations of the law are found because of high residues of DDT than for any other pesticide. One reason why DDT is a continuing problem is the rapidity and extent to which warm-blooded animals store it in their fat. Lactating animals

transfer DDT and other fat-stored pesticides to their milk over a period of time. For this reason no tolerances have been set for such substances in feeds or forage crops intended for dairy cattle. No tolerances have been set for any pesticide residue in milk because no one has yet submitted proof of the safety of any such residue.

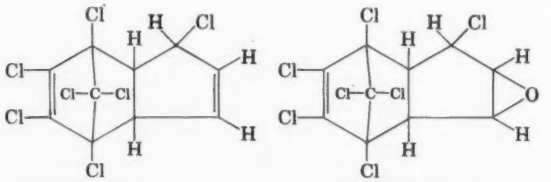
Benzene Hexachloride and Lindane. Benzene hexachloride (BHC) is the common name of a group of isomeric hexachlorocyclohexanes. The technical product contains at least five different stereoisomers; the most important one as an insecticide is the gamma isomer, or lindane. The technical product imparts a musty odor to some crops, but lindane is almost odorless and also is a more effective insecticide.

Aldrin and Related Compounds. The pesticides of this group are all polychloro compounds and contain two fused rings, at least one of which is bridged. They are all very toxic and have low, or zero, tolerances on many crops, as indicated in Table 1. Their discovery dates from 1945. Chlordane, the first of this group to be announced, is an octachloro compound that exists as *cis*- and *trans*-isomers, one of which is considerably less toxic to insects than the other.



Chlordane

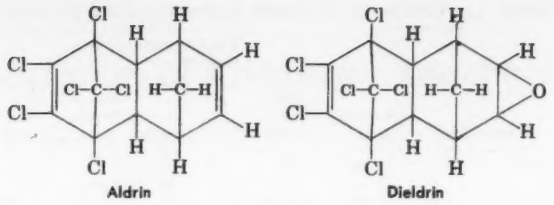
Heptachlor occurs as an impurity in technical chlordane. It is more toxic to most insects than chlordane and is prepared commercially as an insecticide. It is converted to the epoxide on crops, in the soil, and by



animals. The epoxide is stored in the fat and milk of animals, if either the epoxide or heptachlor is ingested (*6*).

Aldrin and dieldrin were first announced in 1948. Both are stable to acids and alkalies, but aldrin can be converted to dieldrin by oxidizing the double bond on the unchlorinated ring. Four structural isomers are possible for aldrin and dieldrin: exo,exo-; exo,endo-; endo,exo-; and endo,endo-. These are described by Frear (*7*). The active principles of these pesticides are the endo,exo-isomers. Endrin, another potent pesticide in this group, is the endo,endo-stereoisomer of dieldrin.

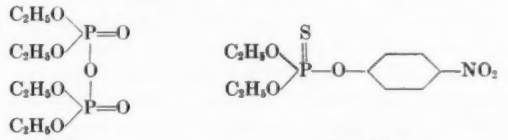
Other Chlorinated Compounds. In addition to those mentioned above, there are a number of other organic chloride pesticides for which tolerances have been set. Among the more commonly used of these are toxaphene, chlorbenzide, Sulphenone, Kelthane, Perthane, Chlorobenzilate, ovex, and Tedion.



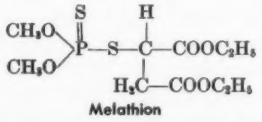
Organic Phosphorus Insecticides

The pioneer development work on this group of insecticides was done by Gerhard Schrader, a German chemist, prior to and during World War II. He was engaged in a study of chemical warfare agents, but his experience with insecticides led him to test some of the new organic phosphorus compounds against aphids. Most of these compounds are highly toxic to warm-blooded animals as well as insects. They act as inhibitors of cholinesterase, an enzyme in nerve tissue that catalyzes the hydrolysis of acetylcholine. Since this reaction is essential to the proper functioning of the nerves, these compounds are powerful nerve poisons.

Tetraethyl pyrophosphate (TEPP) was the first of these compounds to be used commercially as an insecticide. It is highly toxic, and its use on food crops is permitted on a no-residue basis. Fortunately, TEPP is very rapidly hydrolyzed to nontoxic products in the presence of moisture.



Parathion has been the most widely used of the organic phosphorus pesticides. It is quite toxic and has tolerances of 1 ppm on a number of crops (see Table 1). Several less toxic compounds have been developed. One of these is malathion, which is one of the safest of this group. It is quite extensively used and has tolerances of 8 ppm on a large number of crops.



Methyl parathion and EPN are analogs of parathion. In addition, there are several other organic phosphates of interest, including Systox (demeton), Trithion, Diazinon, Guthion, Delnav, Phosdrin, ethion, and ronnel. Some of these are systemic.

Analytical Methods

Chlorinated Hydrocarbons. A nonspecific method commonly used as a sorting procedure for pesticides in this group is the determination of organically combined chlorine (*8*). Good quantitative results can be obtained if only one pesticide is present and its identity is known. This method is frequently used for many compounds, but special techniques are required in using it for the highly toxic aldrin group because of the small residues usually found.

The Schechter-Haller colorimetric method (*9*, *10*) is

specific for DDT and closely related compounds, including TDE and methoxychlor. A specific colorimetric method for BHC and lindane involves the dechlorination of these compounds to benzene, nitration of the benzene, and colorimetric determination of the nitrobenzene (*11*). These are reliable methods that are used in regulatory work.

Colorimetric methods for chlordane (*12*) and heptachlor (*13*) make use of reagents containing ethanolamine and potassium hydroxide. With modifications, the method for heptachlor can also be applied to heptachlor epoxide (*6*). Methods for aldrin (*14*), dieldrin (*15*), and endrin (*16*), also colorimetric, using phenyl azide as a reagent, are quite sensitive and fairly specific for these pesticides. However, the phenyl azide reagents are troublesome to prepare and to keep for routine work. These last three compounds are stable to alkali, while most other chlorinated pesticides are decomposed by hot alkali solutions. This property is made use of in eliminating other chlorinated compounds as possible interferences in the determination of aldrin, dieldrin, and endrin.

Many of the chlorinated pesticides can be separated, identified, and estimated semi-quantitatively by paper chromatography (*17, 3*). These techniques involve a partitioning between two immiscible solvents. The paper is lightly impregnated with an immobile solvent such as mineral oil, and the compounds to be separated are moved up the paper with a mobile solvent such as a mixture of acetone and water. The pesticides are located on the developed chromatogram by treating the paper with a solution containing silver ions and exposing it to ultraviolet light. The location, size, and intensity of spots obtained from the unknowns, compared to spots from knowns, serve to identify the pesticides and give an estimate of their quantity. The clean-up procedure is a very important factor in paper chromatography, and in some cases the degree to which the extract can be purified without loss is the limiting factor in the sensitivity of this method. This technique is very important as a rapid sorting procedure, and it is used in regulatory work in connection with other specific quantitative methods.

The infrared spectrophotometer is a useful tool for the determination of pesticides, particularly in formulations (*18, 19*). The determination of residues on crops with the usual cells and techniques requires the use of rather large samples, but these may be reduced to reasonable limits by using micro cells (*4*).

Gas chromatography also is used for the quantitative determination of pesticides in formulations (*20, 21*). Thermal conductivity detection sometimes lacks sufficient sensitivity for routine residue analysis. The sensitivity has been increased somewhat through a combination of gas chromatography and infrared spectrophotometry, using a liquid micro cell (*22*). Coulson and co-workers at the Stanford Research Institute claim a 1000-fold increase in sensitivity over thermal conductivity detection by using an automatic coulometric titrator as the detector in gas chromatography (*23*). This detector can be used for both qualitative and quantitative determinations of pesticides containing chlorine and sulfur. It should prove to be quite useful for rapid, routine determination of chlorinated compounds.

Organic Phosphates. The ability of the organic phosphates to inhibit the action of the enzyme cholinesterase (CHE) forms the basis for a quantitative determination. An early method (*24*) measures only the *in vitro* inhibitors, which do not include the thiophosphates. Later, it was shown that the thiophosphates could be converted to *in vitro* inhibitors and determined by first treating them with dilute bromine water (*25*). Blood plasma, standardized with acetylcholine, is used as a source of CHE. Some degree of specificity can be obtained with this method (*26*). Oxidized parathion, methyl parathion, and malathion differ greatly in their ability to inhibit the enzyme from different sources. Of eight enzyme systems tried, the three pesticides show most similarity in their effect on rat brain. The difference in activity is less than a factor of three. They show the largest spread in activity in their effects on rat plasma: parathion is 10 times more effective than methyl parathion and about 1000 times more effective than malathion. Thus, these three pesticides can be identified by making two separate inhibition determinations for each, one with rat brain and one with rat plasma as enzyme sources.

There are specific chemical methods for some of the organic phosphate pesticides. Parathion and its analogs, for example, can be determined by a colorimetric method in which the residues are reduced with zinc, diazotized, and coupled with N-(1-naphthyl)-ethylenediamine to produce a color that is measured at 565 mμ (*27*).

The techniques for the separation and identification of 11 different organophosphate pesticides by paper partition chromatography have been worked out (*28*). Several different solvent systems are used, as well as both one- and two-dimensional chromatography. The big hurdle in applying this technique to crop residues is the development of new and satisfactory methods for purification of the sample extracts.

Biological Assay. Bio-assays are useful as fairly rapid sorting procedures and as quantitative methods when a specific pesticide is known to be present. The most commonly used test organisms are *Drosophila melanogaster* (vinegar fly) and *Musca domestica* (housefly). The larvae of *Aedes aegypti* (yellow-fever mosquito), *Daphnia* (water flea) (*29*), and goldfish (*30*), are also used. The percentage mortality of the test organism after exposure to the unknown residue is a measure of the amount of pesticide present.

In one method, applicable to phosphates and chlorinated organics, sugar solutions containing residues extracted from samples are fed to houseflies (*31*). It is a more common practice to expose the flies to a purified sample extract deposited as a film on the bottom of a flask (*32*). The fly bio-assay can be made essentially specific for the aldrin group by taking advantage of their stability to hot alkali (*33*).

The extraction of the insecticide from crops may be eliminated by exposing vinegar flies directly to macerated samples (*34*). The sensitivity of this method varies with the crop and the pesticide, but less than 0.1 ppm of aldrin or dieldrin can be detected on several vegetables.

The fly bio-assay has been made specific for the organic phosphate compounds that inhibit the action of CHE *in vivo* (*35*). The uninhibited CHE is measured on water extracts of flies exposed to the unknown and of

unexposed control flies. The inhibition caused by the unknown is found by comparing the two values. This procedure is sensitive to between 0.5 and 1.0 microgram of parathion. Reasonably good correlations have been found between per cent mortality and per cent inhibition of CHE for nine different organic phosphates (*36*). Exposure of flies to the pesticide residue for only 10 minutes causes almost as much inhibition of CHE as does a 20-hour exposure, even though the short exposure produces no visible toxic symptoms.

A combination of fly bio-assay and paper chromatographic techniques, suitably systematized, may prove to be rapid and useful for regulatory control work.

Regulatory Work

For many of the regulatory samples obtained by FDA for analysis, some information about the spray history of the sample is available. This may be specific information about a particular sample, or it may be only general knowledge of the pesticides that were used in the area in which the sample was grown. In order to keep informed of current practices in the industry, Food and Drug Inspectors make frequent trips through the major producing areas during the growing and harvesting seasons. They visit growers, packers and shippers, pesticide suppliers and applicators, and local officials, and obtain information as to the pesticides that are being used and the frequency of their use.

During a trip last year through one of the lettuce growing areas of Southern California, a Food and Drug Inspector heard rumors that a field of lettuce had been contaminated accidentally with endrin. He made an investigation, assisted by a County Agricultural Inspector, and learned that a hose had broken on an Airplane while the operator was spraying a potato field. Two nearby fields of lettuce, totaling about 46 acres, had been rather heavily contaminated with endrin. The lettuce in one of the fields was being harvested, and about 1,200 cartons had been packed for shipment. As a result of the joint investigation, the harvesting was stopped, and the packed lettuce was not shipped. Local authorities had a 24-hour guard posted around the fields to prevent anyone from being poisoned by taking and eating some of the lettuce. Eventually all of the lettuce involved, valued at $79,000, was destroyed. This was a real potential hazard; several workers handling the lettuce were made ill.

Another FDA inspector working in Arizona found a field of cabbage ready for harvest that had been heavily sprayed in error by an aerial applicator with a mixture of DDT and toxaphene. This field, valued at $3,000, also was destroyed as a result of the FDA investigation. These two incidents illustrate how the vigilance of Food and Drug Inspectors has kept potentially dangerous foods from reaching the markets.

At another time an inspector learned that a lettuce grower was spraying his crop too frequently and too heavily with DDT. Seizures were made after analyses of samples from interstate shipments showed DDT residues greatly in excess of the legal tolerance of 7 ppm. Usually when high residues are found on crops, investigations reveal that the growers have exceeded recommended spray schedules in some manner, either spraying too frequently or too near the harvest date.

The use of most pesticides involves potential hazards. The most practical means of control of these hazards appear to lie in the use of approved practices in applying the potent pesticides. Notwithstanding the fact that a number of seizures of high residue crops are made each year, only a very small percentage of samples analyzed by FDA show residues above the tolerances. The combined efforts of growers, packers, and County, State, and Federal officials help assure a safe food supply.

Literature Cited

(1) Frear, Donald E. H., "Chemistry of the Pesticides," 3rd ed., D. Van Nostrand Company, Inc., New York, 1955, p. 141.
(2) Munro, J. A., *J. Econ. Entomol.*, **39**, 274 (1946).
(3) Mills, Paul A., *J. Assoc. Offic. Agr. Chemists*, **42**, 734 (1959).
(4) McMaulley, D. F., and Cook, J. W., *J. Assoc. Offic. Agr. Chemists*, **43**, 710 (1960).
(5) Frear, Donald E. H., *op. cit.*, p. 11.
(6) Storherr, Robert W., and Tighe, John F., *J. Assoc. Offic. Agr. Chemists*, **43**, 731 (1960).
(7) Frear, Donald E. H., *op. cit.*, pp. 62–66.
(8) "Official Methods of Analysis of the Association of Official Agricultural Chemists," 9th ed., Association of Official Agricultural Chemists, Washington 4, D. C., 1960, p. 342.
(9) *Ibid.*, p. 343.
(10) Schechter, Milton S., et al., *Ind. Eng. Chem., Anal. Ed.*, **17**, 704 (1945).
(11) Schechter, Milton S., and Hornstein, Irwin, *Anal. Chem.*, **24**, 544 (1952).
(12) Davidow, Bernard, *J. Assoc. Offic. Agr. Chemists*, **33**, 886 (1950).
(13) Polen, Percy B., and Silverman, Paul, *Anal. Chem.*, **24**, 733 (1952).
(14) O'Donnell, A. E., et al., *J. Agr. Food Chem.*, **2**, 573 (1954).
(15) O'Donnell, A. E., et al., *J. Agr. Food Chem.*, **3**, 757 (1955).
(16) Bann, J. M., et al., *J. Agr. Food Chem.*, **6**, 196 (1958).
(17) Mitchell, Lloyd C., *J. Assoc. Offic. Agr. Chemists*, **40**, 999 (1957).
(18) Heagy, A. B., *J. Assoc. Offic. Agr. Chemists*, **43**, 342 (1960).
(19) Bunger, William B., and Richburg, Rex W., *J. Agr. Food Chem.*, **5**, 127 (1957).
(20) Zweig, Gunter, and Archer, T. E., *J. Agr. Food Chem.*, **8**, 190 (1960).
(21) Coulson, Dale M., Cavanagh, Leonard A., and Stuart, Janet, *J. Agr. Food Chem.*, **7**, 250 (1959).
(22) Zweig, Gunter, et al., *J. Agr. Food Chem.*, **8**, 403 (1960).
(23) Coulson, Dale M., et al., *J. Agr. Food Chem.*, **8**, 399 (1960).
(24) Giang, Paul A., and Hall, S. A., *Anal. Chem.*, **23**, 1830 (1951).
(25) Fallscheer, H. O., and Cook, J. W., *J. Assoc. Offic. Agr. Chemists*, **39**, 691 (1956).
(26) McCaulley, Jane, and Cook, J. W., *J. Assoc. Offic. Agr. Chemists*, **42**, 197 (1959).
(27) Averell, P. R., and Norris, M. V., *Anal. Chem.*, **20**, 753 (1948).
(28) Mitchell, Lloyd C., *J. Assoc. Offic. Agr. Chemists*, **43**, 810 (1960).
(29) Needham, P. H., *Analyst*, **85**, 792 (1960).
(30) Davidow, Bernard, and Sabatino, F. J., *J. Assoc. Offic. Agr. Chemists*, **37**, 902 (1954).
(31) Frawley, John P., et al., *J. Assoc. Offic. Agr. Chemists*, **35**, 741 (1952).
(32) Tighe, John F., *J. Assoc. Offic. Agr. Chemists*, **43**, 82 (1960).
(33) Klein, A. K., et al., *J. Assoc. Offic. Agr. Chemists*, **39**, 242 (1956).
(34) Earle, N. W., et al., *J. Assoc. Offic. Agr. Chemists*, **42**, 586 (1959).
(35) Frawley, John P., et al., *J. Assoc. Offic. Agr. Chemists*, **35**, 745 (1952).
(36) McCaulley, D. F., and Cook, J. W., *J. Assoc. Offic. Agr. Chemists*, **42**, 200 (1959).

Report of the New England Association of Chemistry Teachers

Lewis Katz
The University of Connecticut
Storrs

A Systematic Way to Avoid Le Chatelier's Principle in Chemical Reactions

In his discussion of the Principle of Le Chatelier and Braun, de Heer[1] presents clear arguments to support the contentions of earlier writers that the principle in its usual formulation is vague and ambiguous. De Heer presents new, valid formulations based on thermodynamic principles. His new statements, however, are expressed in terms and based on arguments which are probably unsuitable for undergraduate presentation, even, possibly, the usual first course in physical chemistry. For the freshman chemistry course, limited statements about the effects of temperature changes and isothermal pressure changes are useful. In addition, most teachers would like to discuss the effect of adding a component to a reaction mixture. Unfortunately the problem here is complicated, because one cannot guarantee, for example, that the addition of a reactant to a reaction mixture at equilibrium will cause the equilibrium to shift to the product side.

In this paper we present an approach intended primarily for undergraduate physical chemistry courses. Our method essentially involves a more rational use of equilibrium constant expressions. This approach, like de Heer's general formulation, is based on thermodynamic principles.

For simplicity, let us consider ideal gas reactions. We may imply a general gas phase reaction by writing:

$$a\mathrm{A(g)} + b\mathrm{B(g)} = e\mathrm{E(g)} + f\mathrm{F(g)}$$

Let us define the symbol Q_P by

$$Q_P = (P_E^e P_F^f)/(P_A^a P_B^b) \tag{1}$$

where the P's are the partial pressures of the substances identified by the subscripts. (The partial pressure of a gas may be taken as its mole fraction, X, times the total pressure.) Similarly, Q_X is the same function as Q_P but with mole fractions substituted for partial pressures; Q_n is the function in terms of the numbers of moles; Q_C in terms of molar concentrations. Thus, for example, Q_n is given by:

$$Q_n = (n_E^e n_F^f)/(n_A^a n_B^b) \tag{2}$$

Let $\Delta\nu$ be the difference in the numbers of moles of (gaseous) products and reactants, i.e.:

$$\Delta\nu = e + f - a - b \tag{3}$$

[1] DE HEER, J., J. CHEM. EDUC., **34**, 375 (1957).

and let n_T be the total number of moles, including nonreacting species. Then the following equations involving the equilibrium constants K_P and K_C hold *at equilibrium:*

$$K_P = Q_P = Q_X P^{\Delta\nu} = Q_n P^{\Delta\nu}/n_T^{\Delta\nu} \tag{4}$$

$$K_C = Q_C = Q_n/V^{\Delta\nu} \tag{5}$$

When the system is not at equilibrium, of course, the K_P and K_C equations do not hold, and conversely.

Let us begin with the system at equilibrium so that the K_P and K_C equations *do* hold. *If the equilibrium is upset, and the K_P and K_C equations are therefore upset, we can predict the direction of the reaction which follows as the one which restores the equalities.* This is our guiding principle, and there is no ambiguity in its meaning. The problem, of course, is to determine the direction of the inequalities which a given change may create, and then to determine in which direction the reaction must go in order to restore the equalities.

In order to apply the above principle we should note that Q_n necessarily increases when the reaction proceeds to the right, and is necessarily decreased when the reaction proceeds to the left. Q_X also increases when the reaction proceeds to the right and decreases when the reaction proceeds to the left, but since this is not so obvious, let us simply accept it at this point and reserve the proof for Appendix 1. In principle, all our arguments could be based on any one of the K_P or K_C equations of (4) and (5). However, the equation which is most convenient in one case is not necessarily the most convenient in another.

For the ideal gas reactions we are considering, K_P and K_C depend only on temperature. (Even for heterogeneous equilibria the equilibrium constants are not very sensitive to changes in pressure and volume.) Let us consider some isothermal cases first. For these cases, then, K_P and K_C remain fixed.

Isothermal Conditions

A. Addition of Inert Gas at Constant Pressure. Of the equations in (4) consider:

$$K_P = Q_n P^{\Delta\nu}/n_T^{\Delta\nu} \tag{6}$$

Addition of an inert gas increases n_T. If $\Delta\nu$ is positive, reaction must proceed to the right so as to increase Q_n and restore the equality. If $\Delta\nu$ is negative, reaction will proceed to the left. If $\Delta\nu$ is zero, there will be no effect on the position of equilibrium.

B. Addition of Inert Gas at Constant Volume. The equation from (5):

$$K_C = Q_n/V^{\Delta\nu} \qquad (7)$$

is the most convenient one to use. Since Q_n is not affected by the addition, and V is held constant, the equality (and the equilibrium) is not disturbed.

(Were we to use the equation (6) in this case we would note that even though n_T is increased, the ratio

$$P/n_T = RT/V$$

is not changed. Therefore, since Q_n is also unchanged, the equilibrium is not disturbed.)

C. Increasing the Pressure by Reducing the Volume (Piston Arrangement). Equations (6) and (7) are both convenient. Consider equation (6). If $\Delta\nu$ is positive, the pressure increase makes $P^{\Delta\nu}$ larger. Reaction will proceed to the left so as to decrease Q_n and to restore the equality. If $\Delta\nu$ is negative, the reaction must go to the right; and if $\Delta\nu$ is zero, the position of equilibrium is unchanged.[2]

D. Addition of Some Reactant or Product at Constant Volume. Consider equation (7). Addition of a reactant decreases Q_n. Reaction would have to go to the right in order to increase Q_n and reestablish the equalities. In general, addition of a reactant at constant volume shifts the equilibrium to the right; a product to the left.

E. Addition of Some Reactant or Product at Constant Pressure. The reaction

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

used by de Heer in his discussion will serve as an illustration, although a number of others would serve equally well. For this reaction $\Delta\nu = 2$. Let us consider the equations (4) as they apply to this reaction and examine the effects of adding the various components. At equilibrium:

$$K_P = (n_{N_2} n_{H_2}{}^3 P^2)/n_{NH_3}{}^2 n_T{}^2 \qquad (8)$$

Addition of NH_3 increases n_{NH_3} and n_T. Both increases serve to decrease the right side of the equation. Reaction must therefore proceed to the right so as to reestablish the equality.

Addition of some H_2 increases n_{H_2} in the numerator, but at the same time increases n_T in the denominator by the same absolute amount. However, since n_{H_2} is necessarily smaller than n_T, the percentage increase in n_{H_2} is larger than in n_T. The fact that n_{H_2} is raised to a higher power than n_T accentuates the positive effect. The effect of adding H_2 therefore is to increase the right side of the equation. Reaction must therefore proceed to the left to restore the equality.

In a similar fashion, the addition of N_2 increases n_{N_2} in the numerator and n_T in the denominator. Again, the percentage increase in n_{N_2} is greater than that for n_T. However, n_T is squared whereas n_{N_2} is raised only to the first power. The effect on the right side of the equation of adding N_2 is certainly not obvious. By the time students take physical chemistry, the natural way to determine this effect on the right side of equation (8), which is Q_P, is to evaluate the derivative with respect to n_{N_2} at constant P. This derivative is found to be:

$$(\partial Q_P/\partial n_{N_2})_P = [(n_{H_2}{}^3 P^2)/(n_{NH_3}{}^2 n_T{}^3)](n_T{}^2 - 2n_{N_2} n_T) \qquad (9)$$

Thus the derivative is positive when $n_T > 2n_{N_2}$, or $X_{N_2} < 1/2$, and negative when $X_{N_2} > 1/2$. This says that Q_P increases with the addition of N_2 when the mole fraction of N_2 is less than $1/2$. The reaction would then have to proceed to the left to re-establish equilibrium. However, Q_P *decreases* with the addition of N_2 when the mole fraction of N_2 is *greater* than $1/2$. Then the equilibrium would have to shift to the *right* when more N_2 is added. To be sure, in most instances, even at constant pressure, the addition of a reactant would shift the equilibrium to the right and the addition of a product would shift the equilibrium to the left. However the exception cited is not unique. A more general evaluation of the effect on Q_P of adding reactants or products at constant pressure is given in Appendix 2.

Non-isothermal Conditions

If the temperature is changed, the values for K_P and K_C will generally be altered. If K_P is increased at constant pressure, it is clear that Q_X must increase to re-establish the equality; this will be accomplished by the reaction proceeding to the right. If K_C is increased at constant volume, it is clear that Q_n must increase; this too is accomplished by the reaction proceeding to the right. The decision about the effect on the equilibrium constants of changing the temperature is made from the equations:

$$(\partial \ln K_P/\partial T)_P = \Delta H^\circ/RT^2 \qquad (10)$$

and

$$(\partial \ln K_C/\partial T)_V = \Delta E^\circ/RT^2 \qquad (11)$$

From the previous expressions for K_P and K_C it is thus clear that an increase in temperature at constant pressure or at constant volume causes reaction to proceed in the endothermic direction. A possible complication in the application of this statement is that the direction which is endothermic at constant pressure is not necessarily the direction which is endothermic at constant volume. This may be appreciated from the well-known, albeit approximate, relationship:

$$\Delta H = \Delta E + \Delta\nu RT \qquad (12)$$

In order for a difference in sign of ΔH and ΔE to occur, however, both would have to be small, thus making the equilibrium constants relatively insensitive to changes in temperature.

Appendix 1

We wish to show that Q_X necessarily increases as reaction proceeds to the right and decreases as reaction proceeds to the left. This conclusion will be demonstrated if we can show that dQ_X/dx is positive, where x is the degree to which the reaction has proceeded to the right. For the reaction:

$$aA(g) + bB(g) = eE(g) + fF(g)$$

Q_X is given by:

$$Q_X = (n_E{}^e n_F{}^f)/(n_A{}^a n_B{}^b n_T{}^{\Delta\nu}) \qquad (13)$$

Taking the natural logarithm of both sides:

$$\ln Q_X = e \ln n_E + f \ln n_F - a \ln n_A - b \ln n_B - \Delta\nu \ln n_T \qquad (14)$$

[2] Cases *B* and *C* emphasize the necessity for being specific about the manner in which a change is made. In these two cases we have had to be specific about the way in which a pressure change was brought about.

$$d \ln Q_X/dx = (e/n_E)(dn_E/dx) + (f/n_F)(dn_F/dx) - (a/n_A)(dn_A/dx) - (b/n_B)(dn_B/dx) - (\Delta\nu/n_T)(dn_T/dx) \quad (15)$$

Now:

$$dn_E = edx;\ dn_F = fdx;\ dn_A = -adx;\ dn_B = -bdx;\ dn_T = \Delta\nu dx \quad (16)$$

Therefore:

$$dQ_X/dx = Q_X[e^2/n_E + f^2/n_F + a^2/n_A + b^2/n_B - \Delta\nu^2/n_T] \quad (17)$$

Thus dQ_X/dx is positive if:

$$e^2/n_E + f^2/n_F + a^2/n_A + b^2/n_B > (e + f - a - b)^2/(n_E + n_F + n_A + n_B) \quad (18)$$

This inequality will certainly hold if:

$$e^2/n_E + f^2/n_F \geq (e + f)^2/(n_E + n_F) \quad (19)$$

To see that (19) would be sufficient to insure (18) one need only observe that the left side of (19) is less than the left side of (18) and the right side of (19) is greater than the right side of (18).

To demonstrate that (19) holds we may multiply both sides by $n_E n_F(n_E + n_F)$. This clears fractions and, after simplification, leaves us with the problem of deciding whether:

$$e^2 n_F^2 + f^2 n_E^2 \geq 2\, efn_E n_F \quad (20)$$

This question is the same as asking whether:

$$e^2 n_F^2 + f^2 n_E^2 - 2\, efn_E n_F = (en_F - fn_E)^2 \geq 0 \quad (21)$$

Since we have a squared number on the left hand side, it must always be equal to or greater than zero, and the direction of the inequalities is established all along the line.

Although we have shown that for the reaction with two products Q_X necessarily increases as reaction proceeds to the right and decreases as reaction proceeds to the left, it may be argued that this does not guarantee the same result for a reaction with a different number of products. However if one tries the above procedure for other reactions one finds that the terms can still be grouped so that quantities which can only be positive or zero are summed to give a result which is necessarily positive or zero. This result in turn establishes dQ_X/dx as positive.

A compact mathematical procedure for generalizing the desired result depends on establishing the general validity of the expression:

$$Z_1^2/Y_1 + Z_2^2/Y_2 + \ldots \geq (Z_1 + Z_2 + \ldots)^2/(Y_1 + Y_2 + \ldots) \quad (22)$$

Using summation signs, the relation to establish is:

$$\sum_{i=1}^{k} Z_i^2/Y_i \geq \left(\sum_{i=1}^{k} Z_i\right)^2 \Big/ \sum_{i=1}^{k} Y_i \quad (23)$$

We have already proved this relation for $k = 2$. The general truth of the relation can be established by induction on the number k. The procedure is to assume the statement for k and show that it would then follow for $k + 1$. Since it is obvious for $k = 1$, and we have proved it for $k = 2$, it is true for all k.

$$\sum_{i=1}^{k+1} Z_i^2/Y_i = \sum_{i=1}^{k} Z_i^2/Y_i + Z_{k+1}^2/Y_{k+1} \quad (24)$$

Since we have assumed (23) for k we may write:

$$\sum_{i=1}^{k} Z_i^2/Y_i + Z_{k+1}^2/Y_{k+1} \geq \left(\sum_{i=1}^{k} Z_i\right)^2 \Big/ \sum_{i=1}^{k} Y_i + Z_{k+1}^2/Y_{k+1} \quad (25)$$

Since we have already established the two term case it follows that:

$$\left(\sum_{i=1}^{k} Z_i\right)^2 \Big/ \sum_{i=1}^{k} Y_i + Z_{k+1}^2/Y_{k+1} \geq \left(\sum_{i=1}^{k+1} Z_i\right)^2 \Big/ \sum_{i=1}^{k+1} Y_i \quad (26)$$

Thus, by assuming (23) for k, the relations (24) through (26) establish the truth of the relation for $k + 1$. According to the previously stated induction argument, then, the truth for all positive, integral k is established. We are thus justified in concluding that Q_X necessarily increases as reaction proceeds to the right and decreases as reaction proceeds to the left.

Appendix 2

In order to examine more generally the effect of adding reactants or products at constant pressure we wish to determine the sign of $(\partial Q_P/\partial n_i)_P$. When this derivative is positive for a product, the addition of that product will increase Q_P, and the equilibrium position will shift to the reactant side. However, when the derivative is negative for a product, addition of that product will decrease Q_P, and the equilibrium position will then shift to the product side. Analogous statements, but with opposite signs for the "expected" and "unexpected" situations, may be made for reactants.

Consider for example, product E. We can show that:

$$(\partial Q_P/\partial n_E)_P = P^{\Delta\nu} Q_X(e/n_E - \Delta\nu/n_T) \quad (27)$$

Therefore the derivative is positive if:

$$\Delta\nu X_E < e \quad (28)$$

But the derivative is negative if:

$$\Delta\nu X_E > e \quad (29)$$

The coefficients and $\Delta\nu$ may be taken as integral without loss of generality. Possible situations for which the derivative would be negative include:

$\Delta\nu$	e	X_E greater than
2	1	$1/2$
3	1	$1/3$
3	2	$2/3$
4	1	$1/4$
4	2	$1/2$
4	3	$3/4$

. . . etc.

Thus, in the heterogeneous reaction:

$$NH_2COONH_4(s) = 2NH_3(g) + CO_2(g)$$

$\Delta\nu$ is 3. The coefficient for CO_2 is 1. Therefore, if:

$$X_{CO_2} > 1/3 \quad (30)$$

adding CO_2 at constant pressure would cause the reaction to go to the right, forming more CO_2. For NH_3 the coefficient is 2, so if:

$$X_{NH_3} > 2/3 \quad (31)$$

adding NH_3 at constant pressure would cause the reaction to go to the right, and more NH_3 would be formed.

If we consider, for example, reactant A, a similar analysis can be made. The derivative, $(\partial Q_P/\partial n_A)_P$, will be positive if:

$$\Delta\nu\, X_A < -a \quad (32)$$

When (32) holds, then, addition of reactant A at constant pressure would lead to the formation of more A.

New England Association of Chemistry Teachers
Officers for 1961–62

President:	Leallyn B. Clapp Brown University
Vice President:	Guy F. Burrill Keene High School
Financial Secretary:	Richard M. Whitney Roxbury Latin School
Recording Secretary:	Mary-Alice Moore Stonehill College
Treasurer:	Carroll B. Gustafson Massachusetts College of Pharmacy
Curator:	Ralph E. Keirstead Connecticut Dept. of Education
Auditor:	Laurence S. Foster Watertown Arsenal
Endowment Fund Trustee: (for three years)	Elbert C. Weaver Phillips Academy, Andover
Nominating Committee Member: (for three years)	Norman G. Mills Wachusett Regional High School
Chairman of Divisions:	
Central:	Harry G. Stubbs Milton Academy
Northern:	Christie Drago Exeter High School
Western:	Angela M. Trovato Branford High School
Southern:	Erich A. O'D. Taylor Portsmouth Priory School

At the Executive Committee Meeting on May 12, 1961, Robert D. Eddy of Tufts University, Medford, Mass., was elected to Honorary Membership.

Chem Ed

LETTERS

To the Editor:

In connection with the article on "The Existence of Endothermic Adsorption,"[1] I should like to call attention to a note recently published in the *Journal of Polymer Science.*[2]

This note deals with the heat of aqueous immersion of polymers. It was found that the heat of immersion in the case of polystyrene was endothermic, and the following quotation is noteworthy:

> The case of polystyrene is surprising inasmuch as reaction with water is unlikely and purification was quite extensive. It is possible, therefore, that this is a genuine case of absorption of heat on immersion. This could be accounted for as follows The heat of immersion of 1 cm² of interface is given by
>
> $$h_{I(SL)} = g_{I(SL)} + Ts_{I(SL)}$$
>
> where $h_{I(SL)}$ is the heat, $g_{I(SL)}$ the free energy, and $s_{I(SL)}$ the entropy of immersion. As the process is spontaneous, the free energy will decrease; hence, in order to obtain heat absorption, the entropy has to increase on adsorption such that $Ts_{I(SL)} > g_{I(SL)}$.

H. H. G. JELLINEK

ESSEX COLLEGE, ASSUMPTION UNIVERSITY
WINDSOR, ONTARIO, CANADA

[1] THOMAS, J. M., J. CHEM. EDUC., **38**, 138 (1961).

[2] JELLINEK, H. H. G., AND LYNN, E. N., *J. Polymer Sci.*, **45**, 270 (1960).

To the Editor:

As an organic chemist, I have retained as my definition of an empirical formula, "the expression of the quantitative analysis of a pure substance in the form of relative numbers of atomic weights, choosing unity for the least measured atomic component." According to this definition, an example of an empirical formula could be $C_{19.1}H_{29.3}NO_{3.96}$.

The case for avoiding premature rounding off to integers in such a formula is obvious to the organic chemist, who may find that the multiplying integer to convert empirical to molecular formulae may be larger than the usual 1 or 2 of inorganic chemistry. I wonder if others feel as I do that the empirical flavor of the analysis ought also to be retained in definitions used by textbooks in other areas of chemistry?

Reputable texts are giving definitions such as "a representation of the molecular structure of a compound in its simplest atomic ratios" or "shows the relative number of different atoms in the molecule." The latter is almost correct but almost invariably is interpreted by students as implying integers.

P. M. LAUGHTON

CARLETON UNIVERSITY
OTTAWA, CANADA

Chem Ed

BOOK REVIEWS

Radioisotope Experiments for the Chemistry Curriculum

Prepared for the Office of Isotopes Development United States Atomic Energy Commission by Nuclear-Chicago Corporation. Edited by *Norman Radin*, Northwestern University, Evanston Illinois. Figs. and tables. 21 × 27 cm. Paperbound.
Readers may obtain one copy free on request to Nuclear-Chicago Corporation, 333 East Howard Avenue, Des Plaines, Illinois. Multiple copies can be purchased at $2.00 per copy, plus $1.00 per copy for instructor's notes. Available also from the Office of Technical Services, Washington 25, D.C.

Willard S. Libby challenged chemistry teachers several years ago to make the use of radioisotopes in the classroom as commonplace as the use of the balance. Earnest teachers of chemistry have been writing in the pages of THIS JOURNAL reports of their own laboratory experiences with radioisotopes in an attempt to fulfill this challenge. The advent of this booklet, Radioisotope Experiments for the Chemistry Curriculum, promises to quicken the pace with which this challenge is met for any teacher who avails himself of its lucidly presented directions.

The real road block to wider introduction of radioisotope experiments in the chemistry curriculum has been the absence of radioisotope experiments that teach fundamental chemical principles rather than illustrate physics of isotopes. Radin and his group through this publication push aside this road block by presenting a series of experiments which incorporate radioisotope procedures to bring out basic chemical ideas. They recognize plainly that new techniques must find their way into the chemistry curriculum, not so much by pushing out important basic material or by being crowded into the chinks between the classical material, but by being utilized as means for presenting fundamentals. This they have achieved to a remarkable degree through their efforts to create radiochemical experiments suitable for *all* chemistry courses.

Inevitably in any collection of experiments a certain amount of unevenness can be expected. There are teachers who will pass over some of the suggested experiments in this booklet considering them less informative for the student than the corresponding classical experiments. On the other hand every instructor should find here at least one experiment which represents a distinct improvement over any possible classical procedure.

For example, by employing an isotopic analysis technique for the determination of phosphate in rock, co-precipitation is minimized and the time for the experiment is cut considerably. In the section on organic chemistry, radioisotope procedures provide insight into mechanisms as an added dividend of their employment.

Some foresight is required in this matter of introducing radioisotope experiments into the curriculum. Sample preparation techniques, fundamentals of nuclear physics, and acquaintance with the counting apparatus are necessary preliminaries to the successful conduct of these experiments. Just how these preliminaries can be worked out for a class tax the ingenuity, the patience and the resourcefulness of a teacher. "Radioisotope Experiments for the Chemistry Curriculum" provides one very real assist in the form of ten preliminary experiments on GM counting, calibration, and sample preparation procedures.

This booklet and its accompanying instructor's manual promise to hasten the day when the chemical education world realizes the challenge thrown down to them by Dr. Libby.

ROBERT H. MAYBURY
University of Redlands
Redlands, California

About Chemistry

Magnus Pyke. The Macmillan Co., New York, 1960. viii + 219 pp. Figs. and tables. 15 × 22.5 cm. $4.50.

On the second page of this book the author states, "... although no one must expect to be able to turn himself or herself into a qualified chemist by simply reading this book, I think that it is possible at least to set out the logical process of observation and thinking by which the trained chemist, who is heir to all the scientists who have lived before him, is able to do the things we see him doing today." Measured by this yardstick the book is, to a large degree, successful. The title, "About Chemistry," describes the book adequately for it is, by any standard, superficial. One should not hesitate to assign it for reading to a bright seventh grade student. Its greatest value probably will be for junior high or high school students, in spite of the fact that it includes numerous formulas and terms commonly reserved for general chemistry or more advanced chemistry courses. In most respects the subject matter is quite up-to-date. Gas chromatography, Ziegler catalysis for tailored polymers, chemisorption, the nature of the DNA molecule, etc. are described in modern terminology. In contrast, the drawings are poorly done, uninspiring, and uninformative. The format, type, paper, and binding are also poor according to American standards.

Many of the British terms will prove amusing or confusing. Mention of the elements columbium, cassiopeium, and masurium may leave some scientifically literate people wondering when these "new" elements were discovered. A distressing implication is found in the statement made after a description of the operation and use of modern spectrographs "... the operation in fact epitomises the basic procedures of science." Statements such as this in a book to be read primarily by young students and laymen create a false image of science which is detrimental to its true understanding.

The author provides several excellent examples which emphasize the importance of observation, reasoning, and capitalizing on the "lucky accident" in scientific investigation. The story of Griess' discovery of the diazotization process while he was employed in a brewery and the story of the discovery of the techniques necessary for polymerizing ethylene should have beneficial effects on inquiring young minds.

After introductory chapters entitled What Chemistry Is All About and What Things Are Made Of, the book is composed

Reviewed in This Issue

Norman Radin, Editor, Radioisotope Experiments for the Chemistry Curriculum

Magnus Pyke, About Chemistry

Richard D. O'Brien, Toxic Phosphorous Esters

Rudolf Sachtleben and *Armin Hermann*, Von der Alchemie zur Grossynthese. Grosse Chemiker

Istvan Naray-Szabo, Anorganische Chemie. Band 1

J. H. de Boer, Editor, The Mechanism of Heterogeneous Catalysis

Roland S. Young, Editor, Cobalt: Its Chemistry, Metallurgy and Uses

C. R. Buxton and *H. Sheldon Jackson*, Russian for Scientists

of sections dealing with a description of chemical reactions along the lines of unit operations and unit processes; the metallurgy of copper, iron, aluminum, magnesium, and chromium; the chemistry of catalytic processes such as nitrogen fixation, production of sulfuric acid, petroleum cracking, etc; organic chemistry including enzymes, vitamins, and carbohydrates; and an extremely superficial section on atomic structure and nuclear energy.

WILLIAM B. COOK
Montana State College
Bozeman

Toxic Phosphorus Esters

Richard D. O'Brien, New York State College of Agriculture, Cornell University, Ithaca, New York. Academic Press, Inc., New York, 1960. xii + 434 pp. Figs. and tables. 16 × 23.5 cm. $14.50.

Much of the pioneering work on toxic phosphorus esters was conducted in Europe in the development of nerve gases during the Second World War. In the past 15 years there has been a tremendous interest developed in these compounds for pesticide usage. Chemists have been actively synthesizing phosphorus esters whereas relatively little has been done on investigating their biochemistry and physiological properties.

The author has undertaken a comprehensive review of the existing information on the subject. The purpose of the book, as stated by the author, is—"to be a source book on organophosphate research, and to show how our understanding of the events that follow organophosphate poisoning of animals can be understood in terms of events at the molecular level." The author's accomplishment is admirable. Not only has he thoroughly and carefully reviewed his subject, it has been done in such a manner as to be provocative reading. Although his conclusions are not always in agreement with those of co-workers in the field, they are based on a sound knowledge of available information. Also, he attempts to present both sides of every issue. Such controversial situations, of which there are many, point out the inadequacy of our knowledge of the field. The author states, for example, that "the extreme selectivity of some organophosphates for some esterases remain a complete mystery." Until there is a full knowledge of events at the molecular and whole tissue levels, the picture of what happens when whole animals are poisoned by these compounds can not be constructed.

An introductory chapter includes a brief historial account, nomenclature of esterases and organophosphates, and a discussion of the structure and biological significance of cholinesterase. Following is a chapter on nonenzymic reactions, two on enzymic reactions in vitro, one on effects on isolated whole tissues, one each on effects in mammals, insects, and plants respectively, one on selective toxicity, and the last on techniques. The importance of technique cannot be emphasized too strongly, as many of the recorded differences in results can be attributed to variations in methods. In this chapter the author briefly discusses established techniques in radio tracer synthesis and analysis of metabolites, which should be of valuable assistance to the novice.

An appendix on electronic interpretations is included at the end of the book. The author realizes that this section is all too obvious for chemists, but the book is also written for biologists, some of whom may not be thoroughly grounded in chemistry. Although there is a considerable amount of chemistry involved in the discussions throughout the book, the interested biologist should be able to comprehend much of the information presented.

This book fills a definite need, being the first to exclusively and thoroughly treat this subject. Certainly it will be of value to all chemists and biologists with interests in the field and should be available for their perusal. The price is rather high but perhaps necessary in a book with an expected narrow circulation.

ROBERT E. TREECE
Ohio Agricultural Experiment Station
Wooster

Von der Alchemie zur Grossynthese. Grosse Chemiker

Rudolf Sachtleben and *Armin Hermann*, both of Munich. Ernst Battenberg Verlag, Stuttgart, 1960. 178 pp. Portraits, figures, and charts. 19 × 27 cm. DM 24 (linen); DM 38 (morocco).

If the author of a history of chemistry examines every facet and carefully explores every side-road he is fairly certain to end up with a rather dull book that is of interest only to the specialists and the reference librarians. For the teacher, student, and reader-at-large it is far better if the Little Jack Horner procedure is applied, and the plums extracted from the large mass and joined by short explanatory essays to form a tasty digestible dish, which can be enjoyed by almost everyone. This selective method has been successfully employed by the authors of the very pleasant volume under review here.

Both of these authors have had ample experience in presenting scientific information. Dr. Sachtleben has written on a wide variety of chemical topics, especially from the historical viewpoint, and is also well known as the chief of the chemical section of the great Deutsches Museum in Munich (J. CHEM. EDUC. **34**, 283). His collaborator is the author of the companion volume "Grosse Physiker" which is now in its third edition. In both of these books little stress is laid on purely biographical details, in fact for even the greatest men this information is condensed into 3 or 4 lines as a kind of footnote.

As indicated by the title, the volume begins with the medieval period (represented by Paracelsus) and comes down to the present (Walter Reppe). The material is divided into 15 sections, and each section is prefaced by an excellent account of what was accomplished in this particular area. Then a group of men is selected for each section as being the key figures responsible for the notable advance. Each of these notables is then allowed to speak, as it were, i.e. pertinent quotations are given from their crucial publications. In this way, the reader gets his information "straight from the horse's mouth." A notable feature of the volume is the collection of 45 full page likenesses of these "great chemists."

All phases and fields of chemistry are included: theory and practice; organic and inorganic; biochemistry and macromolecular chemistry; discovery of the elements, periodic system, and synthetic elements; plant and animal products; chemotherapy, etc. In other words, the general reader will derive a good idea of the development of the entire realm of chemistry and of the men who brought it to this high state.

Doubtless there will be objections regarding the inclusion of some and the exclusion of others from this "Hall of Fame." A selection of this kind is so subjective in many instances that very few will agree with respect to all the choices. There are a good many Germans in this list; the Americans included are Pauling, Seaborg, Langmuir. Chauvinism has no place in any telling of the history of chemistry but there have been instances in the past when the text was slanted to suit nationalistic propaganda ends. With respect to the present book, almost anyone acquainted with the field could justify the inclusion of more chemists with other national origins.

This is a very useful and handsome book. It is enjoyable and informative. Its reception has been so cordial that a second German edition is already in preparation. Steps are being taken to translate it into English.

RALPH E. OESPER
University of Cincinnati
Cincinnati, Ohio

Anorganische Chemie. Band 1

Istvan Naray-Szabo, Budapest, Hungary Publishing House of the Hungarian Academy of Sciences, Budapest, 1959. 664 pp. Figs. and tables. 18.5 × 24.5 cm. $4.

This is the first of a three volume reference book of inorganic chemistry. In the introduction the author states his purpose to write a good medium sized reference book, more extensive than the usual one volume type but not as extensive as Gmelin and others; he has been successful in this as far as can be judged from the first volume. Under such conditions, it has been necessary to leave out much of the history and occurrence of all but the most important compounds.

Professor Naray-Szabo however has placed emphasis upon presenting in a very condensed tabular form the physical

(*Continued on page A494*)

BOOKS FROM INTERSCIENCE

THE PHYSICAL CHEMISTRY OF SURFACES

by A. W. ADAMSON, *University of Southern California*

A textbook which develops an understanding of the various manifestations of surface phenomena by a logical progression from fundamental physicochemical principles. The earlier chapters develop the theory systematically, and are provided with problems designed to require critical thinking, not the mere substitution into given equations. The later chapters apply the theory to problems of friction and lubrication; wetting; flotation; detergency; emulsions and foams; chemisorption and catalysis. In these, student reports involving some aspect of the literature take the place of problem assignments.

"It is virtually certain to be a vital force in education and professional circles as surface chemistry comes of age. Adamson is to be congratulated for the service he has rendered."—Chemical and Engineering News

1960 642 pages $12.75

ARGON, HELIUM, AND THE RARE GASES IN TWO VOLUMES

edited by GERHARD A. COOK, *Research Laboratory, Linde Company, Division of Union Carbide Corporation*

This comprehensive and up-to-date treatment of the elements of the inert-gas group as a family is especially timely and fills a large gap in the literature. In two volumes, the first will cover the history, occurrence, and physical chemical properties; the second volume will treat the methods of isolating, purifying, and handling the gases—their uses, and methods for the analytical determination of the gases themselves and of their impurities. The editor and contributing authors have designed the book for users of the inert gases, for teachers and students, and for those carrying out research in which one or more of the helium-group gases are involved.

Volume 1: Approx. 435 pages; Volume 2: Approx. 420 pages; September

THE CHEMISTRY AND MODE OF ACTION OF HERBICIDES

by A. S. CRAFTS, *University of California, Davis*

Reflecting the great strides which have been made in the chemical control of weeds in the recent past, the author discusses selective and non-selective herbicides: those which are currently available and those still in the development stage. Each class is analyzed in terms of chemical composition, areas of application, and mode of action. The results achieved through various mixtures of herbicides are also discussed.

1961 274 pages $9.00

SCIENTIFIC RUSSIAN

A TEXTBOOK FOR CLASSES AND SELF-STUDY SECOND EDITION

by JAMES W. PERRY, *University of Arizona*

A clear, concise exposition of the basic principles of Russian grammar, combined with complete and well-organized presentation of details and numerous example phrases and sentences. Revised, reviewed and up-dated—especially those exercises dealing with atomic energy, rocket propulsion and other current topics—this new edition has been entirely re-set for improved legibility. From the reviews of the first edition:

"A well-organized and thorough introduction, designed to prepare students and other persons to read scientific literature published in Russian . . . The book is an outstanding one."—New Technical Books (New York Public Library.)

1961 589 pages $9.50

Send for your examination copy

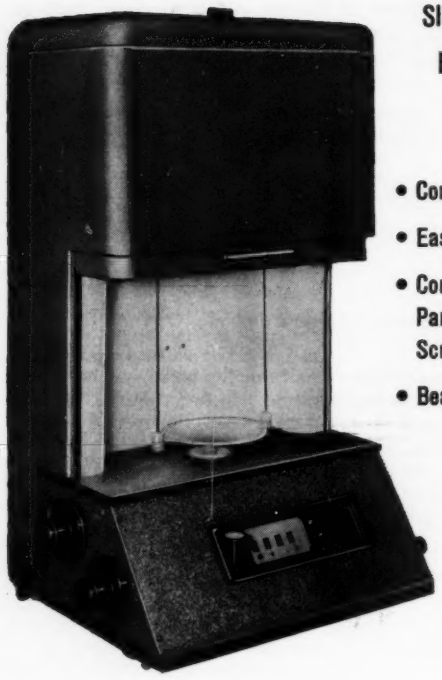
INTERSCIENCE PUBLISHERS, INC.

250 FIFTH AVENUE, NEW YORK 1, N. Y.

BURRELL ... for Balance Satisfaction

STANTON
UNIMATIC

SINGLE PAN
BALANCE



- Complete Weighing In Seconds
- Easy Access Front Opening
- Convenient Grouping Of Controls, Pan, Counter Indicator And Graticule Screen Simplify Operation
- Beautiful Design, Sturdy Construction

The Stanton Unimatic Single Pan Balance, Model CL1, is a completely new precision balance. It is constructed on the constant-load principle thus avoiding errors due to inequality of lever arms, and slight variations in sensitivity due to major changes in load. Synthetic sapphire knives and planes give longer life and the grouped controls at bench level simplify operation.

Features include air damping, full external weight loading to 200 grams without use of loose weights or extra dials plus numerous other important advantages. Cat. No. 2-567-51.... 820.00

... for Balance Satisfaction

BURRELL CORPORATION
SCIENTIFIC INSTRUMENTS AND LABORATORY SUPPLIES
2223 FIFTH AVENUE, PITTSBURGH 19, PA.

BOOK REVIEWS

chemical properties of the elements and their compounds. He also discusses their reactions and their preparation.

Unfortunately most analytical information is omitted; but even more unfortunate only little or no structural information is included. Another serious drawback is the absence of references, aside from the major encyclopedias, textbooks and monograms, most of which are pre-1950.

The first volume is divided into two parts, the first of which (114 pages) is an introduction containing such general topics about the atom as history and development of the periodic tables, quantum theory, electronic configurations, radioactive decay, nuclear reactions, the new synthetic elements, and atomic energy. The treatment is condensed and much important material is left out in line with the author's announced purpose for writing these volumes. The second part of this introduction discusses in about 35 pages the general properties of compounds, including ionic and covalent compounds and their bonding energies, intermetallic compounds, interstitial compounds, hydrates and addition compounds.

The second part of the volume considers the nonmmetals and their compounds. In about 500 pages the author discusses the halogens, the oxygen and sulfur group, the nitrogen group, the elements of group IV_B (silicon, etc.) and finally the compounds of boron. In all of these groups, he leaves out any discussion of the compounds in these groups containing organic substituents since he wants to include no compounds containing nonmetal or metal-carbon bonds. Criticisms might be directed at the fact that much of the work reported in the literature in the last five years has not been included.

This volume should be a *good* reference book for many scientists in chemistry who do not have copies of Gmelin readily available. It should be an *excellent* reference book for scientists in the fields of biology, mineralogy, geology, pharmacology and possibly even scientists in agriculture. One of its excellent features is the presentation of the physical constants of many compounds in tabular form. This volume is bound in a linen cover, the paper seems to be good but the binding itself is not up to quality.

HANS B. JONASSEN
Tulane University
New Orleans, Louisiana

The Mechanism of Heterogeneous Catalysis

Edited by *J. H. de Boer*, Staatsmijnen im Limburg, Geleen, Netherlands. Elsevier Publishing Co. Distributed in the U. S. by D. Van Nostrand Co., Inc., Princeton, New Jersey, 1960. ix + 179 pp. Figs. and tables. 13 × 19 cm. $3.

This small volume constitutes an excellent summary by chemists in Holland of work being done relative to the mecha-

(*Continued on page A496*)

New Chemical Literature from McGRAW-HILL √

☐ PHYSICAL CHEMISTRY

By GORDON M. BARROW, Case Institute of Technology. 720 pages, $8.95.

A modern text prepared with an eye toward unifying the content of physical chemistry by interpreting quantitative chemical behavior in terms of molecular behavior. All physical chemistry is treated from a structural approach, emphasizing the knowledge of the molecular world that can be gained by theory or experiment and the application of this knowledge to the understanding of macroscopic behavior. Problem book available to accompany text.

☐ FUNDAMENTALS OF HEAT TRANSFER

By GROBER, ERK, and GRIGULL; translated from the German by J. R. MOSZYNSKI, Case Institute of Technology. McGraw-Hill Series in Mechanical Engineering. *Available in October, 1961.*

This is a translation of the German classic GRUNDSETZE DER WARMENBERTRAGUNG first published in 1933 and revised in 1955. Apart from its value as a classic in literature, the Third Edition as rewritten by Grigull covers all the fundamentals of the subject and gives a very thorough account of European research in heat transfer up until 1955. Bibliography includes important publications since 1955.

☐ THERMAL REGIMES OF COMBUSTION

By L. A. VULIS; translated from the Russian by GLENN WILLIAMS, Massachusetts Institute of Technology, and others for the project SQUID, Princeton, N. J. Available in July, 1961.

Of primary interest to chemical and mechanical engineers and to chemists and physicists interested in kinetics, this timely translation offers a detailed mathematical discussion of the consequences of applying simple thermal combustion theory and simplified (first order) kinetics to over-all combustion problems. This material is not available in comparable detail in any other English source.

☐ PRINCIPLES OF ORGANIC CHEMISTRY, *Third Edition*

By JAMES ENGLISH and HAROLD CASSIDY, Yale University. Available in August, 1961.

A general revision and up-dating of an established text intended primarily for full-year courses for pre-meds and other non-majors, but also suitable for one semester courses. Avoiding the encyclopedic approach of some texts, the authors have been highly selective and present only those topics necessary to demonstrate basic principles.

☐ THE DETERMINATION OF STABILITY CONSTANTS and Other Equilibrium Constants in Solution

By F. J. C. ROSSOTTI and HAZEL S. ROSSOTTI, University of Edinburgh. McGraw-Hill Series in Advanced Chemistry. *Available in August, 1961.*

A comprehensive guide to the study of complex formation in solution. The material is restricted to a discussion of the experimental and computational methods used to study equilibria in solution. Emphasis is therefore placed on methods to determine equilibrium constants in systems where several species coexist. Concern throughout is focused on the intelligent design of experiments, careful measurements, and rigorous mathematical analysis.

☐ CHEMICAL THERMODYNAMICS

By J. G. KIRKWOOD; and IRWIN OPPENHEIM, Convair Division of General Dynamics. McGraw-Hill Series in Advanced Chemistry. *Available in August, 1961.*

A senior-graduate text with Physical Chemistry prerequisite. The text presents rigorous treatments of gas mixtures and heterogeneous equilibrium and also of electrochemical systems and dielectrics. Contains a new formulation of the Second Law and an important statement of relationship between the Second Law and the Carathedeodory Principle.

Send for copies on approval

McGraw-Hill Book Company, Inc. **330 W. 42nd St., New York 36, N.Y.**

nism of heterogeneous catalysis. It is readable and authoritative. Any chemist wishing to acquaint himself with current problems in catalysis and with the progress that is being made toward solving these problems could do no better than to read this excellent series of papers and the discussions that accompanied their presentation.

The introductory chapter by Professor J. H. de Boer makes clear the meaning of the word "mechanism" as applied to catalytic reactions. It also discusses chemisorption on catalysts, particularly on metallic catalysts; the relationship of such chemisorption to the kinetics of catalytic reactions; the mobility of molecules on surfaces and the selectivity of catalysts.

A very short chapter by Burgers calls attention to some recent work in which he and his colleagues have found at least a qualitative relation between the electronic structure of metal electrodes and redox reactions occuring at the electrodes.

The next three chapters illustrate in detail some recent work concerning the mechanism of the catalytic decomposition of formic acid and the mechanism of ammonia synthesis. These are two reactions which repeatedly have been selected for mechanism studies because of their supposed simplicity. The paper by Fahrenfort, Van Reyen, and Sachtler shows how all of the modern tools of catalytic research can be combined in the study of the mechanism of formic acid decomposition on metals. The interesting conclusion is reached that the reaction proceeds through the formation of metallic formates on the catalyst surfaces. On some metals the rate of formation of the formate is rate determining; on others, such as nickel, the rate of decomposition of the formate appears to be rate determining. This paper, it will be noted, leans heavily on the chemical nature of the catalyst in arriving at a catalytic mechanism.

The activity of metal oxides for the decomposition of formic acid is discussed in detail by Mars. A considerable amount of evidence is given to indicate that the activity of oxides preheated to the same temperature is related to the charge of the cation and also to its radius. Factors influencing the relative amounts of dehydration and dehydrogenation of formic acid for metal oxides are discussed.

The catalytic synthesis of ammonia over iron catalysts has been known for more than 50 years. It is therefore with interest that one notes that even at the end of this period there is no unanimity of opinion in regard to mechanism of this relatively clean-cut catalytic reaction. The paper by Mars, Scholten, and Zwietering presents some interesting recent results which combine to support the traditional idea that the slow step in the rate of ammonia synthesis is the rate at which nitrogen is chemisorbed on metallic iron catalysts. However, they also point out that at the present moment this conclusion as to the rate determining step is disputed by Horiuti and his co-workers in Japan. He insists that one of the steps involving the interaction of hydrogen with nitrogen, NH, or NH_2 groups is a slow step of the reaction. The paper is an excellent illustration of the many different approaches from which the mechanism of a catalytic reaction can be studied.

The next three chapters are concerned with selective catalytic effects in organic reactions. Hoijtink associates preferential effects in the hydrogenation of aromatic ring compounds such as napthalene, anthracene, and phenanthrene with polarization effects of an electrical double layer on the catalyst surface.

Kooyman and Van Helden in discussing a new mechanism for the well known Ziegler polymerization of ethylene suggest that the ethylene molecules add to both ends of the growing chains. A chapter by Coenen calls attention to the importance of the diffusion processes in the selective hydrogenation of various double bonds in fatty oils.

A final chapter by Keulemans and Schuit discusses proposed mechanisms that have been used to account for the action of bifunctional catalysts. These latter are illustrated by the platinum hydroforming catalysts that are currently used in the production of high octane gasoline. They consist of a metallic catalyst supported on a solid having sufficient acid sites to be capable of producing acid catalyzed surface reactions.

This book should be of interest both to

(*Continued on page A498*)

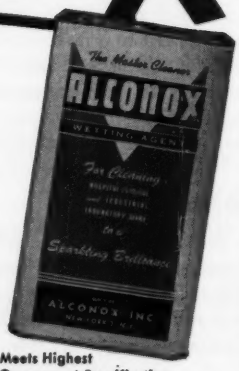
CLEANEST CLEANEST CLEANEST CLEANEST CLEANEST CLEANEST CLEAN
THE
WORLD'S
FINEST
DETERGENT
ALCONOX

Proven the world's finest and most economical detergent for the exacting requirements of Hospital, Medical and Laboratory use.

MEETS HIGHEST U.S. GOVERNMENT SPECIFICATIONS

MORE WETTING POWER!
MORE SEQUESTERING POWER!
MORE EMULSIFYING EFFECT!
QUICKLY, COMPLETELY SOLUBLE AND RINSABLE!

More effective than any known detergent in powder form or any liquid detergent that costs four times as much!



Meets Highest Government Specifications

Sold Throughout the World by
ALL LEADING LABORATORY, HOSPITAL and SURGICAL DEALERS

Also makers of ALCOJET for all equipment washed by machine and ALCOTABS in tablet form for all pipette washers.

Ask your supplier for a copy of the remarkable Alconox Cleaning Guide which may be reproduced for all your students.

ALCONOX, INC., 853 BROADWAY, NEW YORK 3, N.Y.

CHECK MACMILLAN FOR THE BEST IN CHEMISTRY TEXTS

SEMIMICRO LABORATORY EXERCISES IN GENERAL CHEMISTRY

Third Edition

by J. Austin Burrows and Paul Arthur; both, Oklahoma State University; and Otto M. Smith, Kansas State Teachers College

The third edition of this popular manual emphasizes modern principles of chemistry and their application, offering additional quantitative experiments and more opportunities to use the latest techniques and principles. Every experiment has been thoroughly revised and brought up to date, while nine completely new ones introduce students to a variety of topics not commonly included in general chemistry—radioisotopes, paper chromatography, determination of ionization constants, argentimetric titrations, and modern applications of ion exchange resins.

January, 1962

PRINCIPLES AND PRACTICES OF ORGANIC CHEMISTRY

by Frederick G. Bordwell, Northwestern University

This comprehensive text for advanced students emphasizes, for the first time, structure and reaction types rather than functional classes. It provides, however, a thorough training in functional group chemistry, since the behavior of functional classes is reviewed each time new reaction types appear. Over 800 problems require application of principles to new situations, while many introduce new factual material. Facts are stressed throughout, and theory applied only when it is necessary for correlating facts. With essential concepts presented as early as possible and reviewed frequently thereafter, extensive cross-references, and a wealth of information in the footnotes, this book is valuable as both text and reference.

Spring, 1962

GENERAL CHEMISTRY:

A Systematic Approach

Second Edition

by Harry H. Sisler, University of Florida; and Calvin A. VanderWerf and Arthur W. Davidson, both, University of Kansas

Emphasizing the consistent correlation of chemical and physical properties of elements and their compounds with structure, this revised text specifically meets the needs of students who plan to continue their studies in chemistry. Both the theoretical and descriptive sections have been brought up to date to conform with recent advances, and the latest developments in the chemistry of the newer elements, rockets, plastics, and medicine are covered. ". . . an even more usable book for general chemistry classes."—Donald B. Summers, Journal of Chemical Education.

1959 851 pages $7.25

NEWLY REVISED

A SYSTEMATIC LABORATORY COURSE IN GENERAL CHEMISTRY

Second Edition

by Harry H. Sisler and W. T. Lippincott; both, University of Florida; and Jay J. Stewart, E. I. du Pont de Nemours & Co., Inc.

A revised compilation of experiments for freshman courses, this workbook contains more exercises that emphasize quantitative aspects of chemistry and the development and use of mathematical relationships derived from experimental data. Designed for use with most standard introductory texts, this flexibly organized manual offers experiments from a wide variety of topics, allowing instructors to choose their preferred sequence and subject matter. The many experiments give students first-hand experience in developing important equations for predicting behavior of matter.

1961 358 pages $4.00

COLLEGE CHEMISTRY:

A Systematic Approach

Second Edition

by Harry H. Sisler, University of Florida; and Calvin A. VanderWerf and Arthur W. Davidson; both, University of Kansas

The new edition of this well-known introductory text utilizes the structural basis of the properties of matter as its guiding and unifying principle. It presents specific properties of individual elements and compounds as predictable consequences of their atomic, molecular and ionic structure. Featuring a completely new treatment of chemical equilibrium, element-by-element discussion of the synthesis of new elements, and a chapter on rocket fuels, it also explores thoroughly the chemistry of life.

1961 709 pages $7.50

THE CHEMISTRY OF ORGANIC COMPOUNDS

Fifth Edition

by James Bryant Conant, President Emeritus, Harvard University; and Albert Harold Blatt, Queens College (New York)

The latest edition of this basic text offers ample material for a terminal course and provides a good foundation for those who plan advanced work. The effective practice of introducing concepts in relation to their applications has been retained, and the book has been held to the same size. Along with many new illustrations, this edition features changes in both content and format which have been classroom-tested for effectiveness.

1959 652 pages $7.95

The Macmillan Company

60 FIFTH AVENUE, NEW YORK 11, N.Y.

A Division of The Crowell-Collier Publishing Company

SAVE with the ALL NEW Aloe-Petrolite VENTILATED FUME HOOD *Removes fumes without loss of conditioned air.*

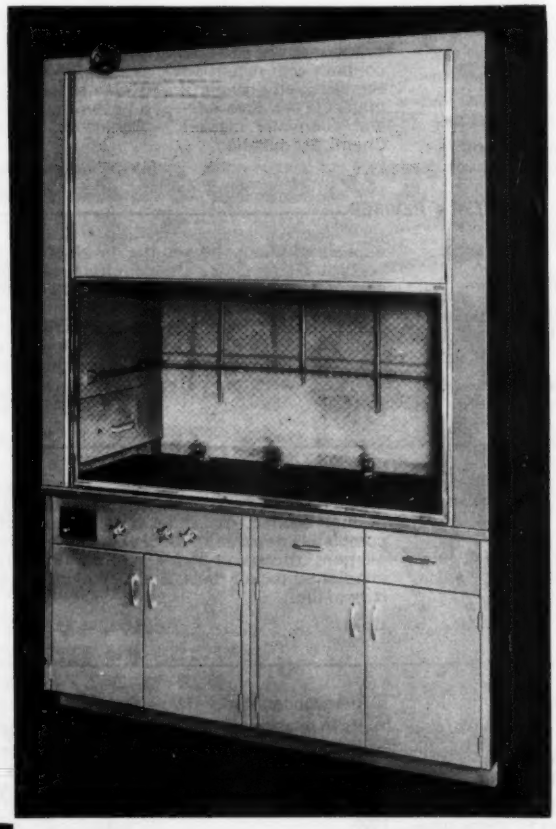
• In addition to protecting laboratory personnel from obnoxious or toxic gases, the Aloe-Petrolite Fume Hood saves conditioned air. Not only in the room where it is installed, but in the entire building. Losing cooled or heated air through fume hoods places an extra load on refrigeration and heating equipment. Result: unnecessary expense. But—by using *outside* air instead of room air, to carry off fumes, waste of conditioned air is stopped. This hood does just that. It operates as an independent unit, completely isolated from rest of room. And in air conditioning savings it can pay for itself.

• **Simple in design**

• **Economical to install**

• **Easy to maintain**

Descriptive bulletin and all details are yours for the asking. Write or call us today.



aloe scientific

DIVISION OF BRUNSWICK CORPORATION

General Offices: 1831 Olive St. • St. Louis 3, Missouri

FULLY STOCKED DIVISIONS COAST-TO-COAST

BOOK REVIEWS

experts in catalysis and to those not specializing in the subject but interested in a quick review of current thinking in the field.

PAUL H. EMMETT
Johns Hopkins University
Baltimore, Maryland

Cobalt: Its Chemistry, Metallurgy and Uses

Edited by *Roland S. Young,* Consulting Chemical Engineer, Victoria, British Columbia. ACS Monograph No. 149. Reinhold Publishing Corp., New York, 1960. vii + 424 pp. Figs. and tables. 15.5 × 23.5 cm. $15.

The tremendously increased activity in chemistry during the last 15 years has made necessary the complete rewriting of much of the chemical literature, including the ACS monograph on cobalt which Dr. Young wrote in 1948. Although the 1960 volume resembles the earlier one in some ways, it is not a revision, but a really new and much larger book. Many of the chapters have no counterparts in the older book; those that do have been completely rewritten and brought up to date.

In the writing of this volume, Dr. Young has had the assistance of several specialists who have written chapters on the fields in which they are expert. The writing throughout is of uniformly high quality and, odd as it may seem for a technical book, this reviewer had trouble in laying the volume aside. The simple cobalt(II) salts are dealt with rather lightly, but the other aspects of the chemistry, metallurgy and uses of cobalt are discussed in an interesting and authoritative way. The chemist who wants to know about the history of cobalt, the optical isomerism of cobalt complexes, the mystery of "salt sick" sheep, the oxo process, the use of cobalt-60 in the diagnosis of pernicious anemia, or the complicated and interesting chemistry involved in the extraction of cobalt from its ores will find the answer here. These examples are but representative bits taken from chapters on the history of cobalt, its complexes, its behavior in biological processes, its uses in catalysis, radioactive cobalt, and the extractive metallurgy of the metal. Other chapters are concerned with the occurrence, properties, and simple salts of cobalt, its phase diagrams and alloys, its applications in magnetic, electric and electronic uses, in tool steels, in cemented carbides, and in ceramics, its electrodeposition and its quantitative determination. Every chapter excites the reader's curiosity and suggests interesting research problems. Even the discussion of the simple salts, which might be thought to be too elementary to be very thought provoking, reports the amazing observation that cobalt(II) iodide exists in two isomeric forms, one of

(Continued on page A500)

Klett . . . .

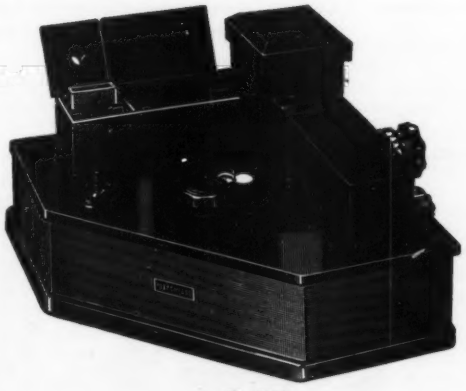
Photometers

Klett-Summerson

Photoelectric Glass Cell Colorimeter

No. 900-3

The Klett Fluorimeter



No. 2070

Designed for the rapid and accurate determination of thiamin, riboflavin, and other substances which fluoresce in solution. The sensitivity and stability are such that it has been found particularly useful in determining very small amounts of these substances.

KLETT SCIENTIFIC PRODUCTS

BIO-COLORIMETERS • GLASS ABSORPTION CELLS
COLORIMETER NEPHELOMETERS • GLASS STANDARDS

Klett Manufacturing Co.

179 EAST 87TH STREET, NEW YORK, N. Y.

ISI PHILA.

Order today

CHEMICAL THERMOMETERS

With porcelain scale (Enclosed Milk Glass Scale) or engraved on stem. In the following ranges:

−10 to 110°C, −10 to 150°C, −5 to 200°C,
−5 to 250°C, −5 to 360°C, 0 to 220°F.

BECKMAN DIFFERENTIAL THERMOMETERS

Reading Upward or Downward. Improved form with auxiliary scale. −10 to 200°C. in 2° divisions, and special "dropping" device to facilitate "setting" each drop of mercury having a definitely rated value in relation to the auxiliary scale. Range 5°C in 1/100° divisions.

ANSCHÜTZ THERMOMETER SETS

Consisting of 7 enclosed scale thermometers each 6" long 6 mm diameter with total range of −10 to 360°C complete in velvet lined case.

Available at lowest prices!

SEND FOR OUR COMPLETE CATALOG

THE INDUSTRIAL & SCIENTIFIC INSTRUMENT COMPANY

5225 GERMANTOWN AVE., PHILADELPHIA 44, PA.

SAFETY ...on tap!

Soothing, diluting water awaits the push of a valve . . . ready to instantly cleanse injured eyes, and at the same time flood facial areas to wash away searing chemicals. Haws emergency equipment means fast, *positive* first aid until medical help arrives. Find out more: write for our new catalog—now!

SINCE 1909 **HAWS EYE/FACE-WASH**

a product of
HAWS DRINKING FAUCET COMPANY
1443 Fourth Street • Berkeley 10, Calif.

EXPORT DEPT.: 19 Columbus Avenue, San Francisco 11, California, U.S.A.

which gives the usual pink solution in water whereas the other dissolves to an almost colorless solution.

Whether this volume is used as a reference, as a source book, or to enrich the teaching of chemistry, it is stimulating and worth while, and every inorganic chemist should have access to it.

JOHN C. BAILAR, JR.
University of Illinois
Urbana

Russian for Scientists

C. R. Buxton and *H. Sheldon Jackson*, University of Manchester, England. Interscience Publishers, Inc., New York, 1960. xix + 299 pp. 14.5 × 22 cm. $5.25.

Language textbooks may be grossly classified into two categories. One type involves the concomitant presentation of grammar, syntax, vocabulary, and reading passages in a gradual progressive manner. The other kind devotes single concentrated sections to grammar, to syntax, to reading passages, etc. The present text is of the latter type; it is divided into five main sections.

The first section (pp. 1–89) is an excellent and detailed listing of the aspects of Russian grammar particularly from the point of view of reading Soviet scientific papers. It does, however, have the following deficiencies: (1) the Russian printed type is rather small, (2) there are no accentuation marks for the Russian words, (3) English transliteration symbols for the Cyrillic alphabet are omitted, and (4) there is deviation from the traditional noun declension order of nominative, genetive, dative, accusative, instrumental, and prepositional cases. The second section (pp. 90–113) is a series of exercises concerned with the application of the previously learned grammatical rules. The authors claim it is "... intended to form a bridge leading from the grammatical section to the annotated texts and the continuous passages." Sentences are given to be translated from the Russian to English and from English to Russian; the correct translations are not provided. The latter exercises are each supplied with an English-Russian vocabulary section. Some ambiguity may be met here since the vocabulary meaning of each word is intended for specific contextual use in the English-Russian exercise. Thus, the word "reduction" is translated as "snizhenie" (p. 113); most chemists, however, would use "vosstanovlenie" as an out-of-context translation for "reduction." The third section (pp. 114–138) deals with the translation of selected annotated technical passages "to facilitate the step from the translation of isolated sentences to that of connected passages." Footnotes are provided with each reading to explain vocabulary and to indicate the relevant part of the first section grammar discussion which applies. Interestingly enough, the title of each of the passages to be translated is in English and not in Russian. The fourth section (pp. 139–200) consists of 92 short passages of technical writings in the fields of physics and electrical engineering, and the fifth section (pp. 201–249) has 75 such passages in chemistry and chemical engineering. Here the student is on his own; there are no footnotes, vocabulary, or correct translation listings. The book is completed by a short list of abbreviations (pp. 250–251), a vocabulary section (pp. 252–296), and an index (pp. 297–299).

The book is well printed, adequately covered, and relatively free of errors. A typographical error appears on p. 20, and misspellings on p. 81 (bezopasnost) and p. 287 (tormoz). The common mistranslation of "tverdykh" as "heavy" instead of "solid" occurs on p. 68. The sound of soft "t" as exemplified by the pronunciation of the letters "tu" in the word "tube" (p. 6) is valid in Britain, but not in America. Two statements concerning the preposition "y" (pp. 81 and 135) appear contradictory.

It is the reviewer's opinion that a student of the scientific aspects of the Russian language should use a gradual, progressive text as his primary source material. The present book is recommended as an interesting supplementary additional text because of its concentrated grammar section and its reading passages.

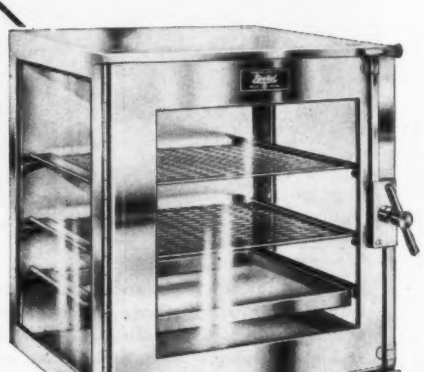
IRVING S. BENGELSDORF
U. S. Borax Research Corporation
Anaheim, California

specify the

Boekel DESICCATING CABINET

for optimum performance in desiccating procedures

THE BOEKEL MODEL 1342, now serving in many metallurgical, chemical, industrial and clinical laboratories, is precisely fabricated of stainless steel, guaranteed air-tight and moisture proof with observation door and sides of 3/16″ glass securely cemented to frame. The "seal-tight" door has a pure gum rubber gasket and full height hinge. Double action bar-lock provides a positive seal and prevents warping. Pressure or vacuum can be normalized before opening door by use of the manual relief valve. The cabinet is equipped with two stainless steel expanded metal shelves (8″ × 9 3/4″) and a stainless steel desiccant tray (8″ × 9 6/8″). Shelf height is adjustable every 1/2″.



Cat. No. 1342

Inside measurements: 12″ high × 11 1/2″ wide × 10″ deep. Outside measurements: 12 1/4″ high × 12 1/2″ wide × 12 1/4″ deep.

● *and now available*—A LARGER DESICCATING CABINET
Size 16″ wide x 22″ high x 20½″ deep (inside dimensions)—designed for use in processing ELECTRONIC COMPONENTS such as TRANSISTORS, MICRO-CONDENSERS and SEMI-CONDUCTORS.
Write for further information.

202

BOEKEL PRODUCTS ARE KNOWN BY THE TRADE MARK (B) DISTRIBUTED THROUGH LABORATORY SUPPLY DEALERS

Manufactured by WM. BOEKEL & CO., INC. PHILADELPHIA 6, PA.

a Chem Ed feature

CHEMICAL PROJECTS

Research Ideas for Young Chemists

Compiled by **JAY A. YOUNG**, Kings College, Wilkes-Barre, Penna.
JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

The Grignard Reagent Reaches the Freshman

See KING, W. B., AND BEEL, J. A., *J. Chem. Educ.*, **32**, 146–148 (1955).

The reaction of methylmagnesium iodide with ethyl alcohol yields methane as one of the products. From the known molecular weight of alcohol, the weight of alcohol used in the experiment, and the volume of methane produced at a measured temperature and pressure, it is reasonable to conclude that ethyl alcohol has the structure CH_3CHOH.

Questions:

Using the procedure described, suggest a reasonable molecular structure for other alcohols, such as ethylene glycol, glycerine, propylene glycol, etc. (Determine the molecular weight of the compound selected by measuring its vapor density or by other suitable means.)

Using a suitable modification of the procedure described, suggest a reasonable structure for a different type of compound: a ketone, an amine, an aldehyde, or a carboxylic acid.

Determine the molecular structure of a polyfunctional compound such as urea, morpholine, or aspirin.

Student Experiments on Derivatives of 1,2-diphenylethane

See FIESER, L. F., *J. Chem. Educ.*, **31**, 291–7 (1954).

It is not possible in a brief abstract to convey adequately the depth of interest which this article will engender in any student who is sufficiently conversant with the field of organic chemistry. Unquestionably, this article is outstanding, particularly for the purposes we hope to fullfill in presenting this series to teachers of chemistry. No specific questions will be cited, contrary to our usual custom, since many questions, implicit and explicit, are indicated in the text of the article.

Eight topics are considered, and for each, Dr. Fieser gives his personal comments, in addition to the preparative details:

Reductive Acetylation of Benzil. The two isomers, *cis-* and *trans*-stilbene-α,β,-diol diacetate, that are formed are separable. Reductive acetylation of quinones can be catalyzed by several different substances, any of which could be tried by a student. However, though it can be done safely, *the use of perchloric acid is strongly discouraged*—use some of the other catalysts mentioned.

meso-Hydrobenzoin. In this simple preparation from benzil, the student can study the use of various reducing agents such as sodium amalgam, sodium borohydride, etc. With other suitable modifications, benzoin can be used as the starting material. It is perhaps possible to isolate *dl*-hydrobenzoin from the mother liquor and effect resolution of this *dl*-diol, ultimately, by mechanical separation of the enantiomeric crystals similar to the pattern of Pasteur's classical method.

trans-Stilbene. A special method is described, adapted to a 1–2 gram scale. It would be interesting to compare this method with other preparative procedures for the same compound.

meso-Stilbene Dibromide. Using pyridinium bromide perbromide, *trans*-stilbene is converted to the *meso*-dibromide. Other brominating agents could be used. The properties of this product should be compared with those of the *dl* isomer, discussed below.

Diphenylacetylene. The rate of dehydrobromination depends upon the temperature of refluxing. This effect can be studied or other techniques used to obtain the unsaturated product.

α-Phenylcinnamic Acid. Both the *cis* and *trans* isomers are formed in this synthesis. They can be separated by their difference in solubility in acidic media. This difference is correlated with the sharp difference in pK_a values of each isomer, and would constitute an interesting study in itself.

cis-Stilbene. This compound is prepared from the *cis* isomer of the cinnamic acid derivative, above, by decarboxylation. The rate of decarboxylation depends upon the temperature. The product is not easily purified and characterized as to purity. Purification and characterization constitute an interesting challenge. Decarboxylating agents, other than copper chromite in quinoline, may be used.

dl-Stilbene Dibromide. Bromination of *cis*-stilbene yields *dl*-stilbene dibromide. If crude *cis* isomer is used, some *meso* dibromide is formed from the *trans* isomer that is present in small amount in the crude material.

Since *dl*-stilbene dibromide can be prepared readily from crude *cis*-stilbene, debromination of this compound should occur by *trans* elimination and yield pure *cis*-stilbene. In the discussion following this observation, the existence of a catalytic effect by zinc bromide upon *cis-trans* isomerization of stilbene and other related phenonema raise many more questions, each sufficiently interesting to stimulate many other investigations.

Sequence of Synthesis in the General Organic Laboratory

See LANGE, E. F., TERANISHI, R., AND CHRISTENSEN, B. E., *J. Chem. Educ.*, **32**, 40–41 (1955).

P-xylene is oxidized to terephthalic acid; part of this acid is converted to acid chloride and the methyl ester formed in a following step. The remainder of the terephthalic acid is nitrated, and the nitroterephthalic acid reduced to the amine derivative. From this, 4-quinazolone-7-carboxylic acid is prepared.

Questions:

Compare the ease of oxidation of *p*-xylene to terephthalic acid with the oxidation of toluene to benzoic acid.

Following the same general outline, what other compounds can you prepare, starting with a compound homologous or isomeric with *p*-xylene?

What other compounds can you prepare from 4-quinazolone-7-carboxylic acid?

Dimethylterephthalate is useful in the synthesis of polymers; prepare this compound and determine the conditions necessary for polymerization.

Vapor Pressure Determination

See RADLEY, E. T., *J. Chem. Educ.*, **37**, 35 (1960).

Most measurements of the vapor pressures of liquids require several milliliters of liquid, but it is possible, as Radley shows, to determine the vapor pressure using only a very small amount of liquid. The length of an air column, confined between two globules of mercury in a glass tube (1 or 2 mm i.d.) is measured. A small quantity of volatile liquid is introduced into this air column and, after equilibration, the increased length of the air-vapor column is measured.

Provided the temperature of the glass tube has remained unchanged, the tubing is of uniform bore, the gases are ideal, and some residual liquid (whose volume is neglected) remains in the space between the mercury globules, the vapor pressure of the liquid can be calculated simply from the changes in length of the confined gas column.

Questions:

Select any moderately volatile liquid or solid and determine its vapor pressure at one or more temperatures.

How much error is introduced by neglecting the volume of the liquid which remains, as liquid, within the confined column?

Is it necessary, as Radley suggests, that the initial column length be approximately 40 cm; can a shorter initial length be used without adversely affecting the precision of your determination of vapor pressure?

Within what limits can the diameter of the tube not be uniform throughout its length without affecting the precision of your measurement of vapor pressure?

Radley's procedure requires the use of a very long tube, if vapor pressures over a wide range of temperatures are to be determined. It is possible to measure vapor pressure over a wide range of temperatures by using the apparatus described by Damerell [*J. Chem. Educ.*, **32**, 534 (1955)] in which one end of a short glass capillary tube is fused shut and a small quantity of *liquid* is confined under a mercury globule. For this purpose the short length of tubing, containing the liquid and mercury globule, is placed in a vessel in which the pressure can be adjusted so as to retain the globule in the short capillary tube as the temperature is increased. Measurement of this pressure, of the length of the mercury globule, and of the temperature then yield the necessary data. Design and set up the necessary apparatus and determine the variation of the vapor pressure as a function of temperature for any liquid you select, from its freezing point to its boiling point.

Two Experiments in Spectrophotometry

See PHILLIPS, J. P., *J. Chem. Educ.*, **31**, 81 (1954).

The concentration of a colored solution can be roughly estimated by comparing the intensity of its color with that of another solution of the same solute at a known concentration. For precise evaluation a colorimeter is used; if the experimenter wishes to obtain detailed information, the light absorbing characteristics of the solute are measured at several selected wavelengths, using a spectrometer. The simplest application of these kinds of data yields information concerning the quantity of unknown present, in straightforward quantitative analysis.

If the concentration of a solute can be measured, however, this knowledge can also be used to determine other characteristics. Knowledge of the concentrations of the ionized and unionized species present in several benzoic acid solutions, each at known *p*H, yields sufficient information to calculate the ionization constant of this acid. Many indicators are weak acids or weak bases; their ionization constants can be determined by this method. Many compounds form colored complexes in solution; the formula of the complex may be calculated by taking a series of measurements of the absorbencies of several solutions containing varied, known quantities of the two species forming the colored complex.

These measurements may be made with a spectrophotometer that is sensitive only to visible light or (alternatively and with increased versatility) with a spectrophotometer that is sensitive to light beyond the visible region. Phillips suggests the use of the latter, and it is necessary for the determination of the ionization constant of benzoic acid. But the simpler type of spectrophotometer can be used to determine the ionization constant of a colored indicator or the formula of a colored complex.

Questions

Determine the ionization constant of a colored indicator.

Determine the formula of a soluble colored complex.

Show that the ionization constant of a weak acid varies as the temperature varies.

Does the ionic strength of the solution affect the ionization constant of a weak acid? What reasons can you give for this effect or its absence? Test your explanation by further experimental investigations.

The method of continuous variations can be used in other types of investigations. Demonstrate one or more of these uses.

Stability of a Complex Ion

See KRUGER, P. AND SCHUBERT, J., *J. Chem. Educ.*, **30**, 196–8 (1953).

The stability of a complex ion can be determined in many different ways. In this experiment, the distribution of radioactive strontium between buffered solutions containing varying concentrations of citric acid and a cation exchange resin immersed in these solutions is measured. From these data, the stability quotient of the complex ion formed between strontium ion and citrate ion is calculated. Though the technique is not demanding, application of the principles discussed by Kruger and Schubert to other related questions will require a certain facility with mathematics. Hence the questions listed below will be more interesting to a student who wishes to learn about radioactivity and who also understands the applicability of abstract mathematical concepts to a chemical problem.

Questions:

Carry out the procedure described by Kruger and Schubert. From further experimental work, identify the major sources of error and determine their relative magnitude.

What effect does a variation in temperature or a variation in ionic strength have upon the stability quotient of the strontium-citrate complex ion?

What is the stability quotient of another complex ion, such as the ion formed between calcium or barium ions and anions of an organic acid other than citric acid?

Is the value of the formation quotient of the strontium-citrate complex ion (or of another similar ion) altered when the organic acid is dissolved in a solution of low *p*H, such that not all of the acid is dissociated into ions?

Carry out the procedure described by Kruger and Schubert. Include, in your calculation of the final results, corrections which depend upon complex formation by buffer anions. Calculate formation quotients for the series of complexes with the general formulas MA, MA_2, MA_3, etc.

Can the same procedure, suitably modified, be used to determine the stability quotient of other complex ions, such as those formed between ions of a transition metal and halide ions?

HELLER
ELECTRONIC CONTROLLED
LAB MIXER

Complete with attachments

$90

F.O.B. Las Vegas

- CONSTANT TORQUE
- STEPLESS

VARIABLE DC SPEEDS FROM AC LINES

• Thyratron tubes on the Heller GT-21 controller supply demanded current by converting power in stepless variation to the direct current motor. Assures constant torque as mixes become either viscous or fluid. Variable, reversible motor has direct and gear drive. Armature shaft speed, 0-5000 rpm. Gear shaft 18:1 ratio. Chuck, shafts, 3-step pulley included.

Order from your Laboratory Supply Dealer or write—

GERALD K. HELLER CO.

2673 South Western Street • Las Vegas, Nevada • P. O. Box 4426

Pressure Reaction Apparatus

PARR Series 4500

For bench-scale reactions in 1 or 2 liter, stirrer-type bombs at pressures to 1000 psig. and temperatures to 350° C.

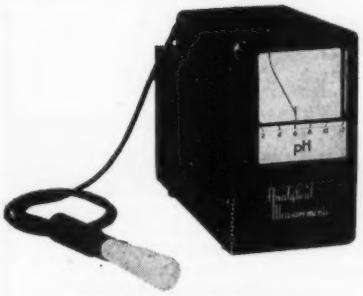
Provides internal stirrer, pressure gage, thermowell, safety rupture disk and convenient fittings for (a) introducing gas, (b) removing liquid samples, and (c) releasing gas without interrupting agitator or heater. Available in T316 stainless steel, also in seven other corrosion-resistant metals and alloys. Internal cooling coils and glass liners can be supplied.

Ask for latest issue of Specification 4500

PARR INSTRUMENT COMPANY

211 Fifty-Third St. Moline, Illinois

pH At Your Fingertips

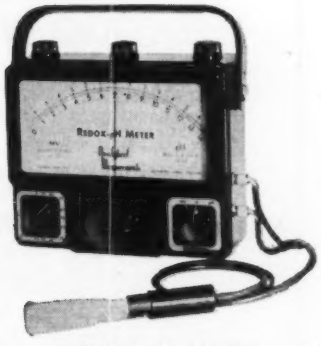


RECORDING pH METER

A pH meter and strip chart recorder in one. Line operated. Simple to operate. Continuously indicating. Write for Bulletin No. 3R.

POCKET pH METER

Battery operated. Completely self contained in water-proof everready case with shoulder strap. Meter scaled 2-12 pH, with simple adjustment for full pH scale. Write for Bulletin No. 100.



REDOX-pH METER

Dual Probe. Line operated. Large 0-14 pH scale. For simultaneous millivolt and pH readings without changing electrodes. Temperature compensator 0-100°C. Write for Bulletin No. 700 MV-pH.

BIG SCALE pH METER

Line operated with protected Analytical pH Probe Unit. Large 7" 0-14 pH scale. One operating control. Write for Bulletin No. 700.

Prices of Analytical pH Meters start at $125.00.

Analytical Measurements, Inc.

585 Main Street Chatham, New Jersey

APPARATUS EQUIPMENT

CHEM ED BUYER'S GUIDE

CHEMICALS SERVICES

Polyethylene WASH BOTTLES

- STURDY, STANDARD LABORATORY WASH BOTTLES
- ONLY PLAX BOTTLES USED
- LEAKPROOF FITTED TUBE well designed tip may be trimmed to suit need
- FINEST WORKMANSHIP
- AVAILABLE AT EVERY LABORATORY SUPPLY HOUSE in U. S. and Canada

No. 203 Standard Capacity	Each	Dozen	Gross
30ml/1 oz.	.41	.37	.33
60ml/2 oz.	.43	.39	.35
125ml/4 oz.	.45	.41	.37
175/6 oz.	.57	.51	.46
250/8 oz.	.65	.59	.53
500/16 oz.	.76	.69	.62
1000/32 oz.	.97	.88	.80

Call Your Laboratory Supply House, Specify #203 Std. Wash Bottles

LPF LABORATORY PLASTICWARE FABRICATORS
714 Baltimore Box 213 Kansas City 5, Missouri

STORE 100 SAMPLES IN 2-¾" SHELF SPACE

Sample Storage Sets

Several Models Indexing Features

Write for Leaflet JCE-SS

CARGILLE 117 Liberty Street New York 6, N. Y.

DEMINERALIZED WATER from TRICKLES to TORRENTS

Plenty of 99.9999% Pure Water For Class Use

CABINET MODEL — up to 100 gals. per hr. houses purifying cell or mixed-bed ion exchange resins. When built-in purity light shows resin exhaustion, purifying cell is returned to factory for regeneration. Greatest convenience and economy. Demineralized water at faucet-flow delivery. D-Ion Master Cat. No. 8120.....$210.00 up

Cat. No. 8120

Write for descriptive literature

ION EXCHANGE PRODUCTS, INC.
4985 N. Elston Chicago 30, Ill.

RARE METALS CHEMICALS

RARE EARTH METAL FOILS

Send for New Lists

A. D. MACKAY, INC.
198 Broadway New York 38, N. Y.

EDUCATORS

Perform realistic science experiments for your classes in Chemistry, Physics, Biology, Botany, Agriculture and Engineering, with Modern Radio ISOTOPES. Now available for the first time in Kit Form. Text Books included. Write for Catalog Dept. CE, VIKING EDUCATIONAL PRODUCTS, 113 S. Edgemont St., Los Angeles 4, Calif.

YOU, TOO, CAN USE

CHEM ED BUYERS' GUIDE

Manufacturers, suppliers, and distributors of chemical laboratory equipment and material, faced with the problem of promoting one or more products which do not lend themselves to inclusion in the company's principal advertisements, or which do not justify the use of more advertising space, find these small units offer just the right size and place for publicizing that *extra* or *special* item. Here is YOUR ideal opportunity to sell that "marginal" or miscellaneous article or that new gadget! Just $12 per inch on a 12 time basis.

NEW and RARE Chemicals

available from our stock

- Aluminum Arsenate C.P.
- Aluminum Cesium Sulfate C.P.
- Aluminum Potassium Fluoride C.P.
- Ammonium Chlorostannate C.P.
- Amygdalin C.P.
- Antimony (ous) Phosphate C.P.
- Antimony Tribromide C.P.
- Barium Benzoate C.P.
- Barium Bromate C.P.
- Barium Dichromate C.P.
- Barium Dithionate C.P.
- Potassium Nitroprusside C.P.

Hundreds of other rare chemicals

Watch for further listings

AMEND
Drug & Chemical Co., Inc.
119 E. 24th St., New York 10, N.Y.

"A biography of one of the immortals in science....."

EDWARD WILLIAMS MORLEY

His Influence on Science in America

by Howard R. Williams

"This is the biography of one of the immortals in science, Edward Williams Morley, professor of chemistry and natural history from 1869 to 1906 at Western Reserve College and University."

"This biography tells not only of scientific achievements but also portrays the character and human qualities of a truly great man. The reader seems to be transplanted to a very different period from today, the nineteenth century. The author writes his story with a feeling of affection and admiration for his subject and in turn this feeling is passed on to the reader. From this biography, the reader will know not only Morley the scientist but also Morley the man."

"This book is recommended to the many who enjoy biography, to chemists and other scientists. Students in high school and college, when the going is sometimes hard, will be inspired in their own work by the examples of Morley's victories over discouragements and by his devotion to scientific pursuits. With its good format, typography and binding, the book might well be a most acceptable gift. It should find a place in all public and school and university libraries as well as on the shelves of most chemists."

NORBERT A. LANGE, Marion Cleaveland Lange
Journal of Chemical Education, March, 1958

293 pages $6.50

CHEMICAL EDUCATION PUBLISHING CO.
Easton, Pennsylvania

SPECIFY **KERN**

When you want to combine accuracy and efficiency in a sturdy instrument at a moderate price . . . specify

KERN

FULL-CIRCLE

POLARIMETER

available through your lab supply dealer

Ask for Bulletin KP 567

KERN COMPANY 5 Beekman St. New York 38

What's new at "EASTERN"?

ARSENAZO • BIBENZYL • BILIRUBIN • SARCOSINE
SULFAMIDE • CYCLOHEXENYL ACETONE • DIPHENYL SULFIDE
p-HYDROXYBENZONITRILE • 3-HYDROXYPIPERIDINE
p-METHYLCYCLOHEXANONE • p-NITROBENZYL ALCOHOL
1-CHLORO-3,3-DIMETHYLBUTANE
1-CHLORO-2,5-DI-n-PROPOXYBENZENE

Inquire for others. We have over 3,000 fine organic chemicals in stock.

EASTERN CHEMICAL CORPORATION 34-A Spring Street Newark 4, N. J.

ANSELL-PLAX

all-polyethylene

WASH BOTTLES

SQUEEZE — THAT'S ALL

Get the stream you want. Can't break . . . won't slip. It's unaffected by strong acids or alkalies. Specified for use by laboratories everywhere —government, institutional, industrial.

ONLY ANSELL-PLAX, FIRST POLYETHYLENE WASH BOTTLE, HAS THE PATENTED* DISPENSING ASSEMBLY THAT MEANS

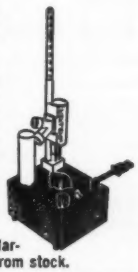
- **NO LEAKING, SEEPING OR NECK SPRAY**
- **QUICK, EASY REMOVAL OF CAP ASSEMBLY**

4, 6, 8, 16 & 32-oz. sizes. Conveniently packed in individual set-up boxes and polyethylene bags. Write us for address of our nearest lab supply house.

*fitment covered by U.S. Patent #2783919

S. H. ANSELL & SON, INC.
825 Summer St., Boston 27, Mass.

MEL-TEMP® . . . an integrated capillary melting point apparatus reaches 400°C effortlessly in only 6 minutes.
MEL-TEMP is useful to 500°C and renders obsolete the usual combination of hazardous fluid-type bath plus sluggish high temperature block. Heater is controlled by variable transformer and excellent viewing is provided by built-in light and lens. Attractive gray hammertone base occupies only 4"x5".



only $97.50 Includes 400°C thermometer and m.p. capillaries. F.O.B. destination in U.S.A. from stock.

Write for Bulletin 60 **LABORATORY DEVICES** P.O. BOX 68, CAMBRIDGE 39, MASS.

- CRYSTAL LATTICE MODELS
- POLYETHYLENE LABWARE
- TEACHING AIDS FOR CHEMISTRY AND PHYSICS

Write for Catalogs

J. KLINGER 82-87 160th Street Jamaica 32, N. Y.

Do You Need:

Cellex Cellulose Ion Exchangers?

(For fractionation of proteins, nucleic acids, and enzymes)

ASK FOR PRICE LIST CCX

BIO-RAD Laboratories

32nd & GRIFFIN AVE. • RICHMOND, CALIFORNIA

SELENOUS ACID
SELENIC ACID
COPPER SELENITE

Some of the many special chemicals we manufacture

Write for our list of rare chemicals

CITY CHEMICAL CORP.
132 W. 22nd St. New York 11, N. Y.

RARE and FINE ORGANICS

o-TOLUALDEHYDE
m-TOLUALDEHYDE
p-TOLUALDEHYDE

o-FLUORO BENZALDEHYDE
m-FLUORO BENZALDEHYDE
p-FLUORO BENZALDEHYDE

o-NITRO BENZALDEHYDE
m-NITRO BENZALDEHYDE
p-NITRO BENZALDEHYDE

o-BROMO BENZALDEHYDE
m-BROMO BENZALDEHYDE
p-BROMO BENZALDEHYDE

Write for Free Catalog #3
#4 is in Preparation Now

K & K LABORATORIES

Incorporated

177-10 93rd Ave., Jamaica 33, N. Y.

Acrylic

LAB-GUARD

WIDE-ANGLE PROTECTION 180°/360°
Send for Catalog

I²R INSTRUMENTS for RESEARCH and INDUSTRY CHELTENHAM, PA.

NEUTRON HOWITZER

GREATER | Capacity Safety Versatility

WRITE FOR DETAILS AND EXPERIMENTS

U. S. NUCLEAR

P.O. BOX 208 BURBANK, CALIF.

WITH **THERM-O-WATCH**— your thermometer becomes a TEMPERATURE CONTROLLER

write for Bulletin P-1

I²R INSTRUMENTS for RESEARCH and INDUSTRY CHELTENHAM, PA.

WITH **THERM-O-WATCH**— your MANOMETER can sound a PRESSURE WARNING! BEEP!

write for Bulletin P-5

I²R INSTRUMENTS for RESEARCH and INDUSTRY CHELTENHAM, PA.

DEPT. JCE
CATALOG NO. CE-302
JC-7

"Keys" such as these are included many times in the advertisements which appear in the *Journal of Chemical Education*. This is done to help the advertiser trace the source of any requests for literature, data, bulletins, and the like. By knowing the exact nature of the original offer, an inquiry can be processed properly.

Be sure to include these "keys" whenever you write for further information . . . better yet . . . mention that you saw the product or service advertised in the *Journal of Chemical Education* and include the date of issue or page number.

By so doing you will insure prompt and correct handling of your inquiry.

What readers say about

SELECTED READINGS IN GENERAL CHEMISTRY

Compiled by **WILLIAM F. KIEFFER**, Editor
Journal of Chemical Education

and **ROBERT K. FITZGEREL**
Kansas Junior College

- ". . . an extremely useful addition to my teaching aids."
- ". . . a fine idea, well conceived and well executed."
- "It has a very good blend of technical articles and articles which give a broad view of chemistry, and it should be of great interest and help to chemistry students and teachers."
- ". . . very interesting . . . a fine start on what could develop into a series."
- "A handsome, interesting and very useful book."

8½" x 11¼ illustrated 128 pages

Single copies..... **$2.00** each
10–19 copies..... **1.75** each
20 or more copies.. **1.50** each
(*all postpaid*)

CHEMICAL EDUCATION PUBLISHING CO.
20th & Northampton Streets • Easton, Pennsylvania

ADVERTISERS' INDEX

Ainsworth & Sons, Inc., Wm. A477
Agency: *Walter L. Schump*
Alconox, Inc. A496
Agency: *Firestone Adv.*
Aloe Scientific Div. of A. S. Aloe Co. ... A498
Agency: *Frank Block Associates*
Analytical Measurements, Inc. A503
Agency: *The Stuart Co.*

Bausch & Lomb Optical Co. ..... OBC
Agency: *Wolff Associates, Inc.*
Boekel & Co., Inc., Wm. A500
Agency: *Lethen Advertising*
Brothers Chemical Co. ..... A468 & A485
Agency: *Ray Ellis Adv., Inc.*
Burrell Corp. A494

Canal Industrial Corp. A464
Agency: *G. Bruce West Adv. Agency, Inc.*
Central Scientific Co. A489
Agency: *Marsteller, Rickard, Gebhardt & Reed, Inc.*
Chem. Ed. Buyers' Guide ..... A504 & A505
Coleman Instruments, Inc. A461
Agency: *Hollander & Weghorn & Morrow*
Coors Porcelain Co. A474
Agency: *Galen E. Broyles Adv.*
Crescent Dental Mfg. Co. A484

DuPont DeNemours & Co., E. I., Industrial & Biochemicals Dept. .. A470
Agency: *Batten, Barton, Durstine & Osborn, Inc.*

Ealing Corp., The A462
Agency: *Randolph Associates*
Eastman Kodak Co. A481
Agency: *The Rumrill Co., Inc.*
Eaton-Dikeman Co. A468
Agency: *Larcom Randall Adv.*
Engis Equipment Co. A467
Agency: *Central Advertising Service*

Fisher Scientific Co. ..... A486 & A487
Agency: *Fuller, Smith & Ross, Inc.*

Gow Mac Instrument Co. A458
Agency: *George Homer Martin Associates*
Greiner Co., Emil A475
Agency: *Fairfax, Inc.*

Haws Drinking Faucet Co. A499
Agency: *Pacific Adv. Staff*
Heller Co., Gerald K. A503
Agency: *The Roman Adv. Agency*

Industrial & Scientific Instrument Co. A499
Interscience Publishers, Inc. A493
Agency: *Henry E. Salloch Adv. Service*

Klett Mfg. Co. A499
Kontes Glass Co. A467
Agency: *The Schurr Co.*

LaPine Scientific Co. A469
Agency: *O'Grady-Anderson, Gray, Inc.*
Lionel/Anton Electronic Laboratories, Div. of Lionel Corp. A460
Agency: *Molesworth Associates*

The Macmillan Co. A497
Agency: *Smith, Henderson & Berey*
Matheson, Coleman & Bell, Inc. A458
Agency: *Leonard M. Sive & Associates, Inc.*
McGraw-Hill Book Co., Inc. A495
Agency: *J. S. Fullerton, Inc.*

Nalge Co., The A471
Agency: *Wolff Associates, Inc.*
Nuclear-Chicago ..... A472 & A473
Agency: *Sidney Clayton & Associates, Inc.*

Ohaus Scale Corp. ..... IFC
Agency: *Robert M. Baldwin Co.*
Olin Mathieson Chemical Corp. A490
Agency: *Doyle, Dane, Bernbach*

Parr Instrument Co. A503
Agency: *F. Willard Hills Adv. Service*
Phoenix Precision Instrument Co. A462 & A476
Agency: *Braun & Miller Adv.*
Pioneer Plastics A488
Agency: *Bridges, Sharp & Associates*
Precision Scientific Co. A465
Agency: *Raymond Wiggers Adv.*

Radiation Instrument Development Laboratory ..... IBC

Sargent & Co., E. H. A456
Agency: *Kreicker & Meloan, Inc.*
Schleicher & Schuell Co., Carl A479
Agency: *Wildrick & Miller, Inc.*
Standard Scientific Supply Corp. A479
Agency: *Firestone Adv. Agency*

Texas Gulf Sulphur Co. A478
Agency: *Sanger-Funnell, Inc.*
Thomas Co., Arthur H. A453
Tracerlab, Inc. A459
Agency: *Culver Adv., Inc., & Walter B. Snow & Staff, Inc.*

U. S. Stoneware Co. A483
Agency: *Ralph Gross Adv., Inc.*

Varian Associates, Instrument Div. ... A480
Agency: *Boland Associates*
Victoreen Instrument Co. A466
Agency: *Palm & Patterson, Inc.*

Welch Scientific Co., The ..... A485 & A492
Agency: *H. A. Hooker Adv.*
Wiley & Sons, John A454
Agency: *Needham & Grohmann*
Wilkens-Anderson Co. A464
Agency: *Mandabach & Simms, Inc.*
Wilkens Instrument & Research, Inc. A482
Agency: *Industrial Literature Service*

Carl Zeiss, Inc. A463
Agency: *John O. Powers Co.*

COMPACT NEW MULTI-PURPOSE

RIDL MODEL 33-8

SINGLE-CHANNEL PULSE HEIGHT ANALYZER

- **Complete unit in a 3-1/2" x 19" chassis**
- **Exceptional accuracy and stability**
- **Fast resolving time**
- **Lock-type RB-dials for drift-free operation**
- **Variable window width**
- **Integral or differential operation at the flip of a switch**

CONTINUOUS IMPROVEMENT through the adoption of printed circuitry and simplified design has made possible this newest analyzer in the RIDL line . . . the compact, versatile 33-8 Single-Channel Pulse Height Analyzer.

TESTED AND PROVEN version of the Oak Ridge Q-1192, the model 33-8 does the work of larger instruments quickly and accurately. It is designed to be used manually or with an electronic sweep such as RIDL model 39-2.

INTEGRAL OR DIFFERENTIAL OPERATION at the flip of a switch! Lock-type RB-dials make sure you stay on channel. Fast resolving time of ½ microseconds reduces dead time to a minimum. Output is negative. Positive output optional from all P.C. boards.

VARIABLE WINDOW, ZERO TO 100%! A major feature of the 33-8. When used with the RIDL model 30-16 Amplifier, the 33-8 Single-Channel Pulse Height Analyzer may be opened to 100% window. The discriminator control on the Amplifier is then used as an upper level. A 20% window on the 33-8 is optional at no extra cost. Window width stability is better than 1%.

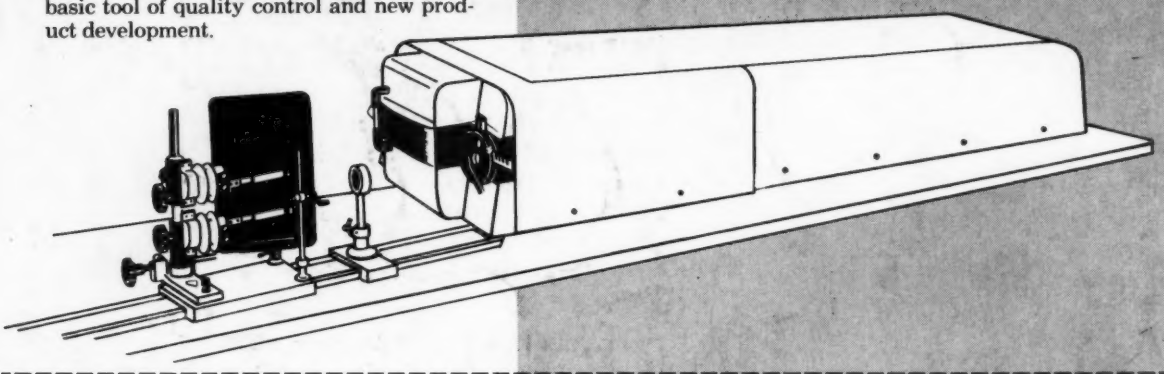
FOR FULL DETAILS: write to Dept. S.

Radiation Instrument Development Laboratory, Inc.

61 EAST NORTH AVENUE • NORTHLAKE, ILLINOIS
PHONE: MUrray 1-2323 • Cable Address: RADILAB

Only $1750! Over $500 less than its closest competitor! But don't let its low cost fool you. In colleges all over the country it's a busy teaching tool, with overtime use in faculty research projects. In industry, it's a basic tool of quality control and new product development.

Bausch & Lomb 1.5 METER STIGMATIC GRATING Spectrograph

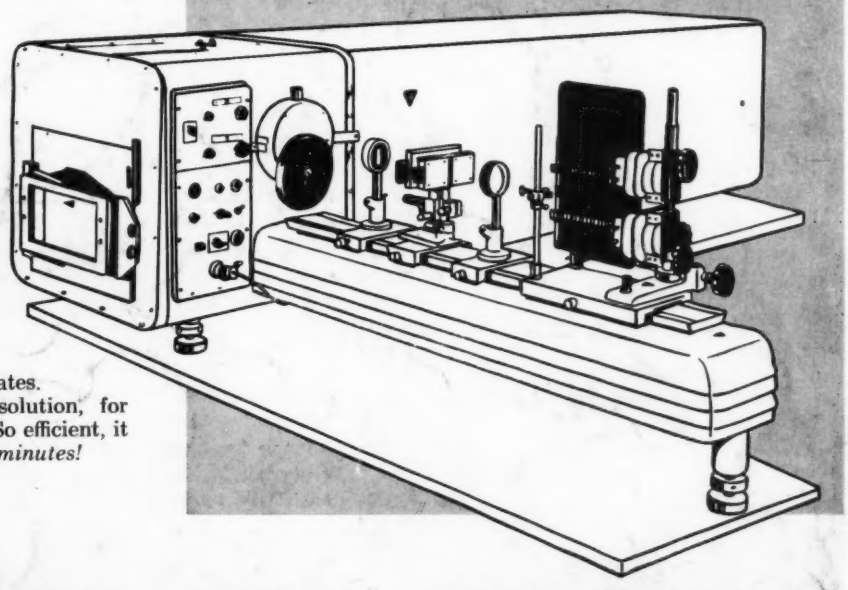


Bausch & Lomb

DUAL-GRATING

Spectrograph

Here's the equivalent of two spectrographs in one! Now you can photograph two different spectral regions . . . in just one exposure . . . on a single 4″ x 10″ plate or two 2″ x 10″ plates. Highest dispersion and resolution, for critical edge-to-edge study. So efficient, it reduces hours of analysis to *minutes!*



How much spectrograph do you really need?

Depends on your work. The more critical, the more you need the high dispersion and resolution of the Dual-Grating. But in more routine use, the simplicity and low cost of the 1.5 Meter make it a popular choice. And there are widely overlapping areas of quality control, education and research in which only your *future* needs can determine which you should choose.

In short, the answer depends on thorough knowledge of your analytical problems and objectives. We'll be glad to survey your requirements—in complete confidence—and recommend the right equipment for your present and *future* needs. Just call us in for consultation at your convenience. No obligation, of course.

BAUSCH & LOMB

Made in America, to the world's highest standards.

BAUSCH & LOMB INCORPORATED
66119 Bausch Street, Rochester 2, N. Y.

☐ Please schedule a consultation at my convenience with no obligation to me.

☐ Please send Spectrograph Catalog D-277.

NAME, TITLE .....

PROFESSIONAL ADDRESS .....

.....